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Dibenzylideneacetone Complexes of Transition Metals

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Information on dibenzylideneacetone complexes of transition metals is reviewed. Their methods of preparation, physicochemical and chemical properties, and also applications as reagents and catalysts are discussed. The bibliography includes 162 references.

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I. INTRODUCTION

Immediately after they were first prepared,[1,2] transition metal complexes with dibenzylideneacetone (DBA) (palladium and platinum complexes in the first place) attracted the attention of both organometallic chemists and synthetic chemists because of their high reactivity and ease of preparation, and the debate concerning their structure continued until 1974 when the structure was reliably established by X-ray structure analysis. DBA complexes of palladium and platinum are now firmly established in the armoury of chemists as convenient starting materials for the preparation of organic derivatives of these metals that are difficult to obtain by other methods, and also as homogeneous catalysts in a great variety of reactions (allylation, nucleophilic addition reactions, alkylation, cross-linking, etc.).

The aim of this review was to survey the available material on the preparation of DBA complexes, especially those of the platinum metals, to show how the formation of complexes with a specific structure (monomeric DBA derivatives, dimeric complexes, solvates of dimers) depends on the preparation conditions used and the reagents, to outline the synthetic possibilities of this class of compound, which is highly reactive, and to summarise the very disjoint information on the use of DBA complexes of palladium and platinum as catalysts. However before doing this it is necessary to discuss the properties of free dibenzylideneacetone which characterise it as a potential ligand.

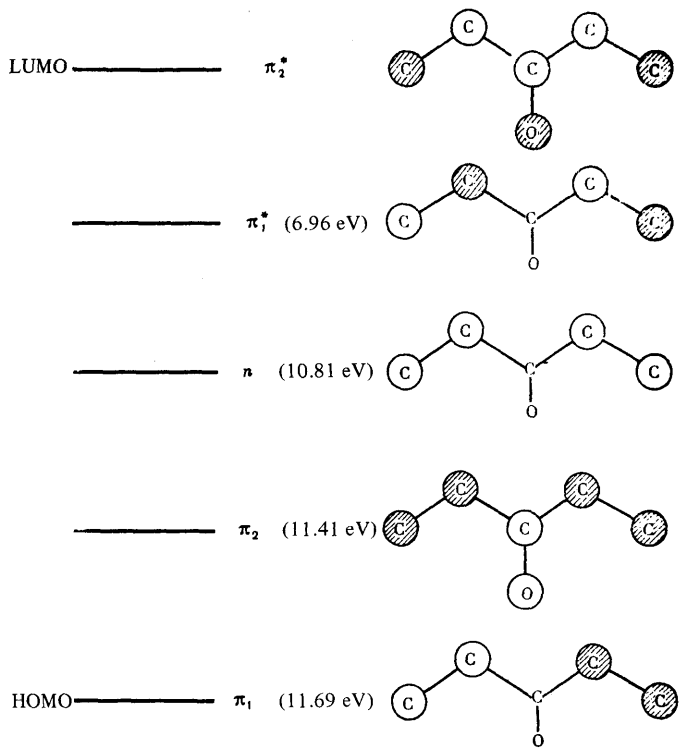


Figure 1. Frontier molecular orbitals of divinyl ketone.

II. DIBENZYLIDENEACETONE AS A LIGAND

To assess DBA as a ligand in complexes with transition metals it is necessary to be aware of its conformational properties and electronic structure because these are controlling factors in coordination. To assess the second factor it is sufficient to have data on the nature of the frontier orbitals, i.e. the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals of the DBA molecule. Such an assessment has been made;[3] the simplest analogue of DBA, divinyl ketone $CH_2=CHCOCH=CH_2$ in the *s-cis,s-cis* conformation, was considered as the model molecule. The energies of the frontier orbitals of the divinyl ketone molecule[3] are shown in Fig.1.

Analogous data for acrolein $CH_2=CHCHO$ [3] and ethylene† are given in Fig.2 for comparison. The HOMO of divinyl ketone is an oxygen p_y-orbital which is a non-bonding AO of the oxygen in the

†The energy of the HOMO of ethylene was taken to be the ionisation energy I = 10.62 eV;[4] the energy of the LUMO was calculated from u.v. spectroscopic data (the energy of the $\pi \rightarrow \pi^*$ transition is 61 000 cm^{-1}).[5]

carbonyl group (the charge on the oxygen, $q_O = 0.82$, agrees well with results obtained by other authors[6]). Its energy (10.81 eV) is similar to the energy of the corresponding MO in acrolein (10.15 eV) but these orbitals have different symmetries; in the acrolein molecule the non-bonding AO of the oxygen in the carbonyl group is oriented along the x axis, i.e. it is a p_x-orbital.

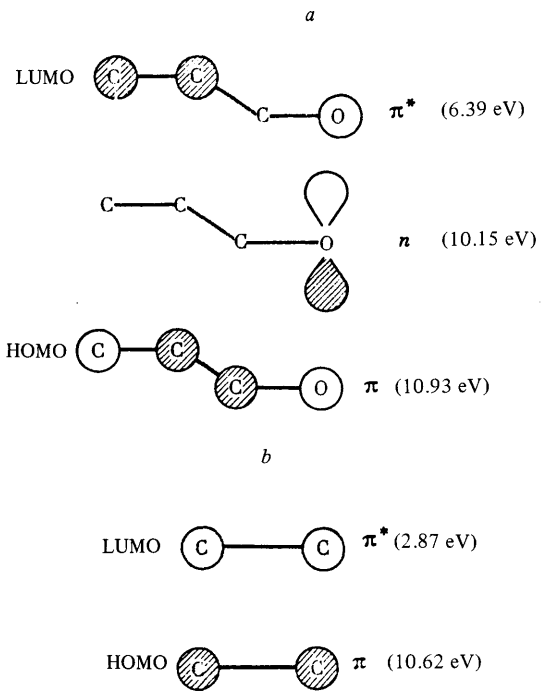


Figure 2. Frontiers molecular orbitals of: *a*) acrolein; *b*) ethylene.

The next occupied MO in the divinyl ketone molecule (and also in acrolein) is the π-bonding MO of the C=C bond with an energy of 11.69 eV (11.76 eV in acrolein); the corresponding antibonding π*-MO's have energies of 6.96 eV for divinyl ketone and 6.39 eV for acrolein. For ethylene the energy of the π-MO is 10.62 eV which is comparable with the energies of the corresponding MO's in divinyl ketone and acrolein; the energy of the lowest π*-MO in ethylene is 2.87 eV which is considerably different from the energy of the corresponding orbitals in divinyl ketone. Hence the formation of a $d \rightarrow \pi^*$ type metal–ligand donor-acceptor back bond, particularly with metals in low oxidation states for which the highest occupied d orbitals have energies in the region of 8 eV,[7] will be energetically more favourable for the two α,β-unsaturated carbnonyl compounds (acrolein and divinyl ketone) than for ethylene. This conclusion agrees with results[8] indicating an increase in the stability of olefinic π-complexes of transition metals in low oxidation state when acceptor substituents are introduced into the olefin molecule.

The most suitable donor orbitals in the divinyl ketone molecule are the n- and π-orbitals and the second are more favourable although their energy is somewhat lower ($\Delta E = 0.9$ eV). As a rule, therefore, in α,β-unsaturated carbonyl compounds the double bond is much more easily coordinated than the carbonyl group. Nevertheless, bidentate coordination, with the α,β-unsaturated ketone forming chelate or bridging complexes, is also possible.[3,8] Hence, *a priori*, for DBA the possibility of both $n \rightarrow d$‡ and $\pi \rightarrow d$ types of coordination cannot be excluded. As will be shown below, both occur.

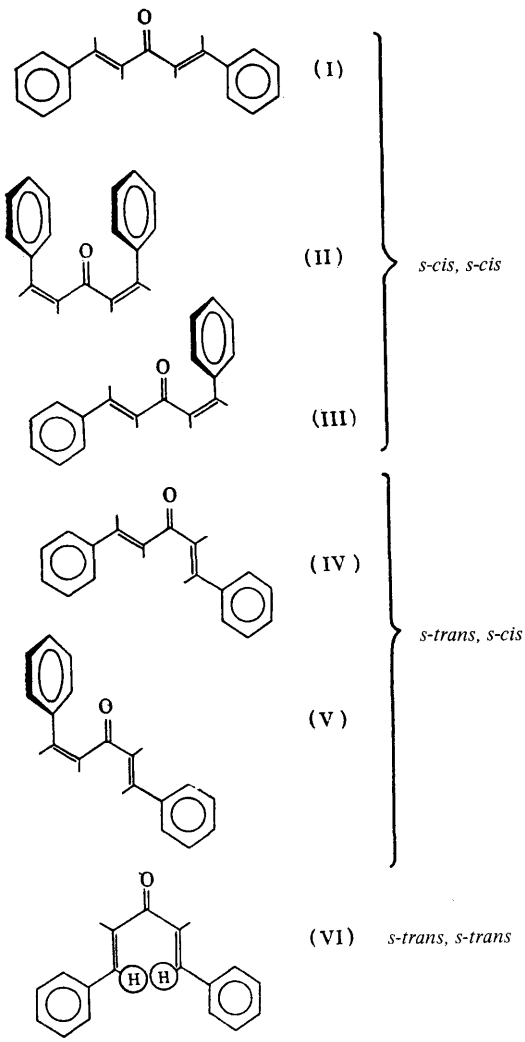


Figure 3. Possible conformations of DBA.

We shall now discuss the conformational properties of DBA. In principle it is possible to have the following alternatives of a planar arrangement of the C=C and C=O bonds relative to each other combined with different configurations of the ethylenic bonds (Fig.3):[9,10] three *s-cis,s-cis* conformations (I, II, and III), two

‡ $n \rightarrow d$-Coordination was assumed for DBA in its complexes with Pd^0 and Pt^0;[2] see also Ref. 3.

s-trans,s-cis (IV and V), and one *s-trans,s-trans* conformation (VI). However, Stuart–Brigleb models and van der Waals diagrams with Stuart–Brigleb radii show that the planar *s-trans,s-trans* structure (VI) is impossible owing to repulsion between the β and β′ hydrogen atoms (the overlap is 1.2 Å); structures I and IV§ are completely planar and hence energetically more favourable [the small overlap (0.21 Å) between the α and β′ hydrogen atoms in structure IV can be disregarded].[12] In structures II, III, and V steric hindrance forces one or both of the phenyl groups out of the plane of the double bonds. U.v.,[12,13] n.m.r.,[14] and i.r. [9] spectroscopic data also indicate that DBA molecules occur in solution only with a *trans* configuration of the two ethylenic bonds. This is also supported by dipole moment data.[14] Thus the conformational characteristics of DBA in solution define it as an olefin in which the two double bonds are unlikely to be coordinated to the same metal atom because they have different symmetries. Coordination of DBA as a 1,4-diene is therefore less favoured and effectively two possibilities remain: DBA acts as a bridging ligand in binuclear complexes or is an ordinary unidentate olefin with somewhat greater potentialities for donor-acceptor back bonding compared to ethylene. How such potentialities are realised will be shown below.

Table 1. U.v. spectra (λ in nm) of DBA, TBAA, and their palladium and platinum complexes.[16,17]

DBA	TBAA	$Pd(DBA)_2$	$Pt(DBA)_2$	$Pd_2(DBA)_3.CHCl_3$	$Pd_3(TBAA)_3.CHCl_3$	Assignment
233 m.	231 m.	235 m.	235 m.	236 m.	234 m.	π→π*
325 s.	320 s.	336 s.	336 s.	300 sh. 321 s.	320 s.	n→π*
374	—	378	—	—	—	unassigned
520 w.	—	538 m.	568 m.	—	—	d→d

Note. s. = strong, m. = medium, w. = weak, sh. = shoulder.

Table 2. I.r. spectra (cm^{-1}) of DBA, TBAA, and their palladium and platinum complexes.[16,17]

DBA	TBAA	Pd $(DBA)_2$	Pt $(DBA)_2$	$Pd_2(DBA)_3.CHCl_3$	$Pd_2[(C_6D_5CH=CH)_2CO]_3.CHCl_3$	$Pd_3(TBAA)_3.CHCl_3$	Assignment
1667 m.sh.	1667 m.sh.	—	—	—	—	—	—
1651 s.	1650 s.	1656	1652	—	—	—	ν(C=O)
1627 m.	1628 m.	1613	1624	1620, 1614 s.	1620, 1615 s.	1620, 1614 s.	$\nu(C=C)_{aliph}$
1591 s.	1591 s.sh.	—	1593	1600 s.	1591 m.	1590 m.	$\nu(C=C)_{arom}$
1574 s.	1575 s.	1579	1579	1574 m.	1550 m.	1575 m.	—
—	—	1544	1527	—	—	—	—
983 s.	981 s.	—	—	975 w.	977 w.	981 w.	$\sigma(CH)_{trans}$

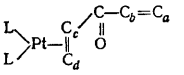
III. THE STRUCTURES OF DBA COMPLEXES OF TRANSITION METALS

As indicated above, in its metal complexes DBA can act as both an *n*- and a π-donor ligand but in the latter case, owing to its conformational characteristics, DBA is less likely to form diene complexes of the chelate type and more likely to act as a uni- or bi-dentate π-olefinic ligand.

The available X-ray structural data indicate that all the possible modes of bonding between DBA and transition metals occur.

However, we shall first discuss the spectroscopic (u.v., i.r., and n.m.r.) properties of DBA complexes.

Table 3. Parameters of the ^{13}C n.m.r. spectra of DBA and $L_2Pt(DBA)$ complexes.[21]



L	C_a	C_b	C_c	C_d	$J(Pt-C_c)$	$J(Pt-C_d)$
PEt_3	124 6	134.8	49.7	61.0	235	180
$AsEt_3$	123.0	135.8	46.3	58.0	275	185
DBA (uncoord.)	135.4	142.7	135.4	142.7	—	—

The u.v. spectra of uncoordinated DBA, the complexes $Pd(DBA)_2$, $Pt(DBA)_2$, and $Pd_2(DBA)_3.CHCl_3$, and also tribenzylideneacetylacetone (TBAA) and $Pd_3(TBAA)_3.CHCl_3$ are compared in Table 1.

It is clear that the bands due to the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions in DBA show no change in either position or intensity on coordination. In the opinion of the authors of Refs.16 and 17 this indicates that the carbonyl group in DBA is not involved in the coordination.

I.r. spectroscopic data for DBA, $Pd(DBA)_2$, $Pt(DBA)_2$, $Pd_2(DBA)_3.CHCl_3$, $Pd_2[(C_6D_5CH=CH)_2CO]_3.CHCl_3$, TBAA, and $Pd_3(TBAA)_3.CHCl_3$ are compared in Table 2.

The conclusions drawn from the i.r. spectra by different authors are very contradictory. The data in Table 3 [Table 2? (Ed. of Translation)] can provide support for coordination both via the carbonyl group and via the C=C double bonds in DBA.

Next we shall consider the n.m.r. spectroscopic data for DBA and its complexes. The similarity between the ^1H n.m.r. spectral characteristics of uncoordinated DBA and complexes of the type $M(DBA)_2$ (M = Pd, Pt) was noted as far back as 1971.[2] In compounds of the type $M_2(DBA)_3$ (M = Pd, Pt) the signals of the olefinic protons in DBA are shifted to low field on coordination with the metal atom.[18,19] ^1H n.m.r. spectroscopic data indicate that only one of the two C=C bonds in DBA is coordinated to the platinum in $L_2Pt(DBA)$ type complexes.[20] This was also confirmed for the complexes $L_2Pd(DBA)$ (L = PPh_3, PEt_3, PPh_2Me, $AsPh_2$, $AsEt_3$) by ^{13}C n.m.r. spectrosocpy (Table 3).[21]

N.m.r. spectroscopic data thus show that the coordination of the DBA is of the $\pi \rightarrow d$ type and the DBA complexes of Pd and Pt can be regarded as π-olefin derivatives of these metals.

The question of the structure of DBA compounds of palladium, platinum, and rhodium was finally resolved by X-ray structure analysis.

Dibenzylideneacetone forms several types of complex: $M(DBA)_2$ (M = Pd, Pt), $M(DBA)_3$ (M = Pd, Pt), $M_2(DBA)_3.Solv$ (M = Pd, Pt), $MO_2Cl_2(DBA)_2$ (M = U), and $C_5Me_5M(DBA)$ (M = Rh). X-Ray structure determinations have been carried out on all these types except $M(DBA)_2$.

§However, measurements of the molar Kerr constants of DBA can be reconciled with an *s-cis,s-cis* conformation only on condition that the phenyl groups are rotated by 26.5° around the 1,4-axes.

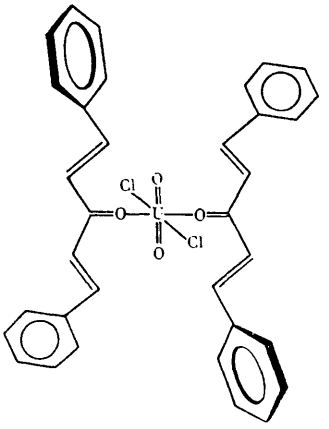


Figure 4. Structure of $UO_2Cl_2(DBA)_2$ in the crystal.

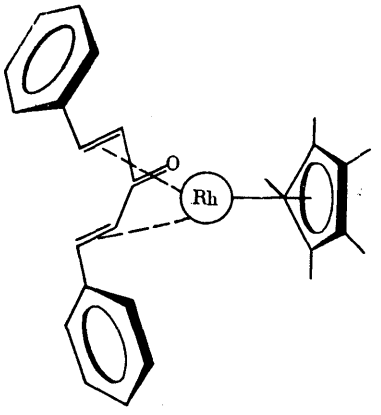


Figure 5. Structure of $C_5Me_5Rh(DBA)$ in the crystal.

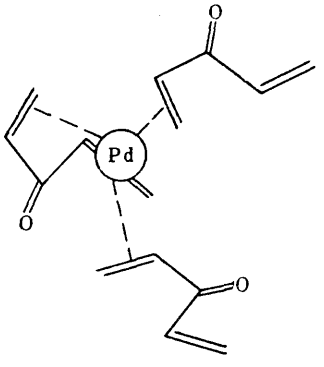


Figure 6. Structure of $Pd(DBA)_3$ in the crystal.

In the uranyl compounds the DBA is coordinated to the uranium atom via the oxygen atom of the carbonyl group (Fig.4);[22-24] the ligand is in the *s-cis,s-cis* conformation and the changes in the C=O and CH=CH bond lengths in DBA owing to coordination are unimportant. The phenyl rings are in the plane formed by the

$$-CH=CH-\overset{\overset{O}{\|}}{C}-CH=CH-,$$

system, i.e. the DBA is in the planar *cis,cis*-form (I) which is energetically the most favourable for uncoordinated DBA.

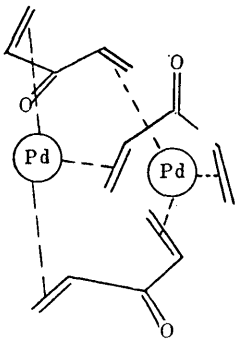


Figure 7. Structure of $Pd_2(DBA)_3.CH_2Cl_2$ in the crystal.

In the rhodium complex (Fig.5) DBA acts as an η^4-dienone ligand.[25,26] The coordinated DBA has the symmetrical *s-trans,s-trans* configuration (VI) which, as has already been mentioned, is impossible for the uncoordinated ligand because of the intramolecular H...H interaction between C(3)H and C(5)H; this distance is 1.2 Å in free DBA and 1.89 Å in the rhodium complex. The DBA molecule in this complex is under considerable strain and this is evidently the reason for the high catalytic activity of $C_5Me_5Rh(DBA)$. Tris(dibenzylideneacetone)palladium (Fig.6) is a tris-olefin complex of Pd^0.[27] Each of the three pentadiene ligands is coordinated by only one C=C bond, the DBA molecule is in the most favourable *s-cis,s-trans* conformation (IV), and the relatively small changes in the DBA bond lengths on coordination reflect the weakness of the metal–ligand bond in these complexes.

In the solvated complexes $Pd_2(DBA)_3.Solv$ the three ligands are bonded to the palladium atoms in different ways depending on the nature of the solvent Solv.[28,29] When Solv = CH_2Cl_2 two of the DBA molecules are in the *s-cis,s-trans* conformation but the third is in the *s-cis,s-cis* form (Fig.7). When Solv = $CHCl_3$ all three DBA ligands are in the *s-cis,s-trans* conformation. The factors determining the conformational properties of the DBA ligands in the $Pd_2(DBA)_3$ complexes are considered[28,29] to include not only the intramolecular contacts in DBA itself but also interligand interactions and, all in all, they will lead to an optimally strong π-bond between the metal and the olefin fragment of the DBA. On these grounds the most favourable DBA conformation will be *s-cis,s-cis*, in which the two C=C fragments are oriented approximately in the trigonal planes of the two Pd atoms. However, this does not provide sufficient separation between the two metal centres. The *s-cis,s-trans* conformation is more suitable from the latter point of view.

The interaction-between-the-metal-atoms factor does not of course apply in "monometallic" complexes but the *s-cis,s-trans* conformation usually still occurs because of the DBA–DBA interligand interactions. However, in (bipy)Pd(DBA), where there are no such interactions, the DBA ligand is in the *s-cis,s-cis* conformation (W-conformation) (Fig.8).[30]

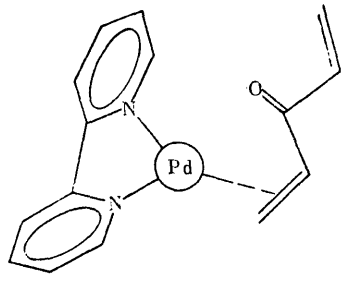


Figure 8. Structure of (bipy)Pd(DBA) in the crystal.

The available experimental data on the strutures of DBA complexes in the crystalline state thus agree fairly well with the preliminary assessments discussed above. The structures of the complexes in solution have been studied by n.m.r. spectroscopy.[31-33]

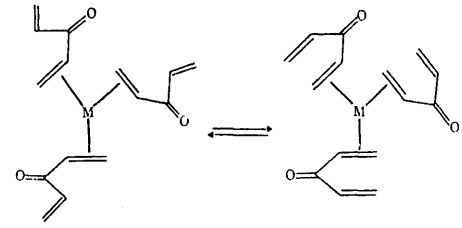
In a $CDCl_3$ solution the $Pd_2(DBA)_3.CHCl_3$ molecule has the three DBA ligands in the *s-cis,s-trans* conformation,[33] as in the crystal. Similarly, the ^1H n.m.r. spectrum of $Pd_2(DBA)_3.CH_2Cl_2$ in CD_2Cl_2 shows that one of the DBA ligands is in the *s-cis,s-cis* form, also agreeing with the X-ray structural results.[29]

There was found to be a linear correlation between the values of J(AB) and δ(H) for the olefinic protons in the DBA ligands. Hence the spin–spin interaction is determined by the same factors as the chemical shift. In the opinion of Kawazura et al.[31] the ability of the ligand to form a donor-acceptor back bond with the metal (π-back-donation) is one such factor. The capability of olefin ligands for back donation in turn depends on two factors: the geometry of the olefin (*cis* or *trans*) and the distance between the metal atoms and the double bond.

From the results of MO calculations for olefinic complexes of nickel[34] with the metal and the C=C bond located in the same plane, *trans*-olefins are more capable of back donation than *cis*-olefins. In the case where all three DBA ligands are in the *s-cis,s-trans* form (the $CHCl_3$ solvate) the mean distances between the Pd and the C=C bond (2.19–2.22 Å) are shorter than in the CH_2Cl_2 solvate where one ligand is in the *s,cis,s-cis* conformation. The interaction of these two trends evidently also determines the structure of the complexes in solution.

For the analogous platinum complex $Pt_2(DBA)_3.CHCl_3$, whose structure has not been determined by X-ray diffraction, ^1H n.m.r. data for a solution in $CDCl_3$ [32] indicate that two of the DBA ligands have the *s-cis,s-trans* conformation and one is in the *s-cis,s-cis* form, as in Ref.31; the connection between J(Pt–H) and the capability of DBA for back donation is discussed.

Studies have been made of the ^1H n.m.r. spectra of $M(DBA)_3$ complexes (M = Pd, Pt) [23] which will be more dynamic in solution as compared to the binuclear $M_2(DBA)_3$ compounds.[27] In $CDCl_3$ at –60 °C all three coordinated DBA ligands have an *s-cis,s-trans* conformation with the *s-trans* fragment of the ligand bonded to the metal atom. On raising the temperature the following equilibrium occurs:



In the Pt complex the amount of the equilibrium form containing the *s-trans,s-trans* ligand may be fairly large. The authors attribute this to more effective back donation in the Pt derivative than in the Pd complex.

Thus DBA complexes of Pd and Pt have the same structure in the crystalline state and in solution. The conformational and energy characteristics of DBA as a potential ligand which were discussed above apply almost totally in its complexes with the platinum metals. In these derivatives DBA acts as an olefin with an electron-accepting substituent and the compounds discussed can be regarded as π-olefin complexes of platinum metals in low oxidation states.[35]

IV. METHODS OF PREPARING DBA COMPLEXES OF TRANSITION METALS

For the preparation of DBA complexes of transition metals only one method, the reaction of an excess of DBA with a metal salt in the presence of a base, is used.[1,2,16,18,21,28,35-39] The reactions are usually carried out in an alcoholic or aqueous-alcoholic solution, with sodium acetate or carbonate as the base.

A second method, the substitution of other ligands by DBA,[39] has no preparative value and is used only to determine the comparative stability of the complexes of palladium with DBA and TBAA.¶

$Pd(DBA)_2$ was first obtained[1] by adding sodium acetate to a methanol solution of a mixture of Na_2PdCl_4 and DBA (DBA/Pd $\geqslant$ 3) heated to 60 °C. Cooling to room temperature gave a brownish black crystalline complex of composition $Pd(DBA)_2$ which is fairly stable in air in the solid state but slowly decomposes in solution depositing palladium metal. This complex is sparingly soluble in CH_2Cl_2, $CHCl_3$, and benzene forming highly coloured solutions.

$Pd(DBA)_2$ was later obtained[37] by adding a hot aqueous solution of K_2PdCl_4 to an alcoholic solution of a three-fold excess of DBA and an eight-fold excess of NaOAc in alcohol in a nitrogen atmosphere. However, the products had different i.r. spectra, as was noted in Ref.28. If the complex obtained by the latter method[37] is recrystallised from $CHCl_3$ or CH_2Cl_2 the product has an i.r. spectrum similar to that of the specimen obtained by the first method.[1] A detailed investigation of the latter showed[18,21] that its recrystallisation from $CHCl_3$ or any other organic solvent gives complexes with the composition $Pd_2(DBA)_3.Solv$, where Solv represents a molecule of the solvent used. A very convenient method for preparing $Pd(DBA)_2$

¶TBAA, PhCH=CHCOC(COCH=CHPh)=CHPh, (m.p. 112 to 113 °C) has an *s-cis,s-trans* conformation according to i.r., u.v., and n.m.r. spectroscopic data.[39]

is the addition of palladium chloride to a hot (~50 °C) methanol solution of a mixture of DBA and AcONa (Pd/DBA/AcONa ratios = 6/20/50).[18] Ater the reaction mixture has been stirred at 40 °C for 4 h a reddish purple precipitate with m.p. 135 °C and the composition $Pd(DBA)_2$ is formed. This is evidently the complex the authors of Refs.1 and 2 were dealing with. Dissolving it in hot chloroform gives a dark violet solution from which purple acicular crystals with m.p. 122–124 °C and the composition $Pd_2(DBA)_3.CHCl_3$ are deposited when ether is added. If $Pd(DBA)_2$ is dissolved in benzene, toluene, or dichloromethane, the corresponding solvates $Pd_2(DBA)_3$.Solv, where Solv = C_6H_6, C_6H_5Me, or CH_2Cl_2, crystallise out.[28] It is interesting that the complexes formed by *p,p'*-dimethoxydibenzylideneacetone[18,21] and *p,p'*-di-isopropyldibenzylideneacetone[25] contain no solvent molecules but have the composition Pd_2L_3, where L is the corresponding DB derivative. Interconversion of the $Pd_2(DBA)_3$.Solv complexes occurs on recrystallisation from the appropriate solvent.[18] However, in the preparation of $Pd_2(DBA)_3$.Solv the use of chloroform is recommended[28] because recrystallisation from this solvent gives the maximum product yield (~80%). The palladium complex with *p,p'*-di-isopropyldibenzylideneacetone mentioned above was obtained by dissolving the PdL_2 initially formed in THF and then adding methanol. It is interesting that in the preparation of tris(di-isopropyldibenzylideneacetone)dipalladium[36] the reagents were mixed in the "reverse" order: anhydrous sodium acetate was added to a hot mixture of DBA and Na_2PdCl_4 in methanol; the yield of the final product was 75%.

TBAA reacts with $PdCl_2$ and AcONa under the conditions described above[18] to form, after recrystallisation from $CHCl_3$, the purple acicular complex $Pd_3(TBAA)_3.CHCl_3$ in an 84% yield.[39] As with DBA, the precipitate formed initially gives the corresponding solvate $Pd_3(TBAA)_3$.Solv on crystallisation from $CHCl_3$, CH_2Cl_2, or benzene. Unfortunately the composition of the initial precipitate was not determined. Like the $Pd_2(DBA)_3$.Solv complexes, the TBAA complexes can be interconverted on recrystallisation from the appropriate solvent.† When the reaction of $PdCl_2$ with TBAA is carried out in cyclohexanol instead of methanol, the cyclohexanol is oxidised to cyclohexanone in an 81% yield calculated on the basis of the palladium chloride used in the reaction.[39]

Another palladium complex with DBA, mononuclear tris(dibenzylideneacetone)palladium, is also known. $Pd(DBA)_3$ can be obtained in two ways: by adding a four-fold excess of DBA to a benzene solution of $Pd_2(DBA)_3.C_6H_6$ [38] or by the reaction of Na_2PdCl_4 with DBA in aqueous alcohol in the absence of sodium acetate.[37] In the first case a mixture of the complex $Pd(DBA)_3$ with free DBA is formed. Chemical analysis of the complex indicates the presence of one molecule of benzene to each molecule of the compound. $Pd(DBA)_3.C_6H_6$ dissociates readily in solution, giving $Pd(DBA)_2$. Thus, taking account of the results from Ref.28, we may conclude that there is a series of DBA complexes of palladium in equilibrium with each other:

$$Pd_2(DBA)_3 \overset{DBA}{\rightleftharpoons} Pd(DBA)_2 \overset{DBA}{\rightleftharpoons} Pd(DBA)_3.$$

A similar mononuclear tris(dibenzylideneacetone)platinum complex has been obtained.[2] It is prepared by boiling K_2PtCl_4 with a three-fold excess of DBA in methanol in the presence of sodium acetate. Air or oxygen must be present but its role is not clear; chemical anlaysis shows that the product contains no "extra" oxygen. Maitlis et al.[36] mention that $Pt(DBA)_2$ is formed by the reaction of K_2PtCl_4 with DBA in the absence of oxygen; however, in later work[37] these authors, referring to methods for preparing $Pt(DBA)_n$ (n = 2, 3), do not mention anything about the determining effect of oxygen or air. A comparison of methods for preparing $Pt(DBA)_2$ and $Pt(DBA)_3$ shows that the latter is formed in a more prolonged reaction (4 h as against 10 min) and at higher DBA/Pt and AcONa/Pt ratios (17/1.2 and 30/1.2 respectively, as against 10/3.6 and 35/3.6). Furthermore $Pt(DBA)_3$ is formed at 40 °C but $Pt(DBA)_2$ in boiling ethanol (~80 °C). The two complexes are very different in colour: $Pt(DBA)_2$ is purplish black and $Pt(DBA)_3$ is canary yellow. The tris-complex dissociates completely to $Pt(DBA)_2$ and free DBA when dissolved in organic solvents;[2] this is indicated by cryoscopic determinations of the molecular weight in benzene. $Pt(DBA)_2$ forms the solvates $Pt_2(DBA)_3$.Solv when it is dissolved in such solvents as C_6H_6, $CHCl_3$, toluene, etc.[19] These results have been confirmed for the platinum complex with *p,p'*-di-isopropyldibenzylideneacetone.[36] The addition of an aqueous solution of K_2PtCl_4 to a boiling solution of NaOAc and *p,p'*-di-isopropyldibenzylideneacetone in ethanol (K_2PtCl_4/NaOAc/di-isopropyl-DBA ratios = 7.2/73.0/15.7) followed by boiling for 1 h gave a black complex of composition PtL_2, where L = *p,p'*-di-isopropyldibenzylideneacetone, which in THF forms a dark purple solution. After evaporation of the solution and the addition of methanol violet-black crystals of composition Pt_2L_3 slowly crystallised out. The complex obtained in Ref.16 is evidently the solvate $Pt_2(DBA)_3.CH_2Cl_2$ and not $Pt(DBA)_2$,[19] because it was produced by crystallising the crude $Pt(DBA)_2$ from dichloromethane. In the same work[16] the mixed complexes $L_2Pt(DBA)$ (L = PPh_3) were obtained by the reaction of L_4Pt with DBA in toluene; this is another example of the preparation of DBA complexes by ligand substitution. Triphenylphosphine is easily displaced from $Pt(PPh_3)_4$ by other α,β-unsaturated olefins;[16] the complexes $(Ph_3P)_2PtL'$, where L' is 4-phenylbut-3-en-2-one or 1,3-diphenylprop-2-en-1-one, were obtained in this way. The spectroscopic properties of these complexes are similar to those of the DBA complexes. It is interesting, in connection with this, that 4-phenylbut-3-en-2-one (benzylideneacetone) forms complexes with Fe^0 which have an η^2-olefinic or η^{1-4} heterodiene structure[17,40–47] depending on the nature of the other ligands bonded to the iron atom. The formation of η^2-olefinic complexes has also been observed in the reaction of 4-methyl-pent-3-en-2-one with the Pt^{II} derivatives K_2PtCl_4 and $(C_2H_4)_2Pt_2Cl_4$;[48,49] with Pd^{II} π-allylic complexes are formed.[50,51]

Thus the DBA complexes with palladium and platinum which were originally thought to have the composition $M(DBA)_2$ in fact have the more complex structure $M_2(DBA)_3$.Solv; another type of DBA complex, $M(DBA)_3$, is also known for palladium and platinum. Finally, there are reports of DBA complexes of rhodium[25] and uranium[22] containing respectively one and two molecules of the ligand per metal atom. The rhodium derivative $Me_5C_5Rh(DBA)$ was obtained[25] by the reaction of di-μ-chloro-bis(pentamethylcyclopentadienylrhodium) with DBA in alcohol in the presence of Na_2CO_3, i.e. by the usual method of preparing DBA complexes of transition metals. The uranium complex $UO_2Cl_2(DBA)_2$ was isolated in the photodimerisation of DBA in the presence of UO_2Cl_2.[22] It has long been known that DBA is dimerised to 1,3-diphenyl-2,4-dicinnamoylcyclobutane by UO_2Cl_2 [52] and $SnCl_4$ [53] whereas photodimerisation in the absence of metal salts gives 1,2-diphenyl-3,4-dicinnamoylcyclobutane.[54] The reaction of DBA with metal salts has also been mentioned elsewhere.[55–59] For

†Hence the scheme given in Ref.18 is also valid for TBAA complexes.

example, under the action of alkali metal alkoxides the semicarbazone of *trans,trans*-DBA cyclises to *cis*- and *trans*-1,2-diphenylcyclopent-3-enes.[55] Five-membered alicyclic compounds are formed by the reaction of DBA with Os^{IV} salts in the presence of Zn dust;[56] reductive dimerisation gives 1-styryl-2-cinnamoyl-3,4-diphenylcyclopentanol in a quantitative yield. Electrochemical reduction of DBA or the action of such reducing agents as Mg and Zn amalgams also lead to reductive dimerisation but the yield of the cyclopentanol mentioned above is very small.[57–59] Similar reductive dimerisation reactions occur in the Os^{IV}–Zn system with other α,β-unsaturated ketones.[56]

V. CHEMICAL PROPERTIES OF DBA COMPLEXES OF TRANSITION METALS

Two types of reaction are characteristic for DBA complexes of transition metals: substitution of the ligands without changing the oxidation state of the central metal atom and oxidative addition which, as a rule, takes place with substituion of the DBA ligands. The reactivity of the palladium compounds has been studied most thoroughly because these compounds are readily available and stable. Note that the kinetic and thermodynamic stabilities of the DBA complexes of Pd and Pt are diametrically opposed. The DBA ligand is the most labile of the known π-ligands[60] because it is easily displaced even by such ligands as acetylenes; however, the thermodynamic stability of DBA complexes of transition metals is comparable with the stability of such strong complexes as the π-allylic complexes. For example, the dissociation energy of the Pt–DBA bond is 273 kJ mol^{-1} [61] which is greater than the corresponding energy of the Pd–π-allyl bond in bis-π-allylpalladium chloride (237 kJ mol^{-1}).

1. Ligand Substitution Reactions

Even in the earliest work on the chemistry of DBA complexes[1,2] the high tendency for coordinated DBA to be replaced by various ligands was noted. The strength of the reaction depends on the nature of the metal atom and the properties of the substituting ligand. A soft base such as triphenylphosphine reacts with tris(dibenzylideneacetone)dipalladium, replacing all the ligands and forming tetrakis(triphenylphosphine)palladium:[18,21] even a large excess of the harder base bipyridyl (bipy) replaces only two DBA molecules on reaction with $Pd_2(DBA)_3$ in acetone, forming the unstable complex (bipy)Pd(DBA).[18,21] Pyridine (py) and *o*-phenanthroline (phen) react similarly. Complete replacement of DBA from the platinum complex $Pt_2(DBA)_3$ occurs only on reaction with the stronger π-acceptor $AsPh_3$ (reagent ratio $AsPh_3$:$Pt_2(DBA)_3$ = 4);[18] reaction with an excess of R_3P (R = Me, Et, Ph) or a deficiency of $AsPh_3$ [$AsPh_3$: $Pt_2(DBA)_3$ = 2] gives the partially substituted products $L_2Pd(DBA)$ (L = PMe_3, PEt_3, PPh_3, $AsPh_3$).[16] These results indicate that the DBA complexes with platinum are more stable and also that the strength of the metal–DBA bond increases with the degree of substitution. This may be due to the stabilising effect of the *n*-donor ligands; however, the results of a thermogravimetric study[18,21] show that the stepwise detachment of DBA ligands from a palladium complex occurs even in the absence of other ligands.

From a practical point of view the reactions of DBA complexes with olefins are the most interesting because they are at present the only method for preparing olefinic π-complexes of Pd^0 of the type L_2Pd(olefin).[62]

(a) Reactions with olefins. $Pd_2(DBA)_3$ reacts with olefins without *n*-donor ligands being present but the olefinic complexes formed have not been isolated because they decompose to palladium metal and free DBA under the reaction conditions used (acetone, room temperature).[18,63,64] Stable (olefin)PdL_n complexes are formed if ligands such as bipy, phen, or $P(OR)_3$ are present in the reaction mixture together with the olefin.[18,63–65] The stability of the complexes formed is determined by both the nature of the olefin and the basicity of the ligand L. Only olefins with electron-accepting substituents form stable complexes; for stable complexes to be formed the lower the π-accepting ability of the olefin the greater must be the σ-donor properties of the ligands. A table showing the effect of the nature of the olefin and the ligand L on the stability of (olefin)PdL_n type complexes has been published.[18,64]

Table 4. Stability of the palladium olefin π-complexes (olefin)PdL_n.[66]

Olefin	*e*	L					
		bipy	phen	tmeda *	$P(OPh)_3$	$P(OMe)_3$	PPh_3
Maleic anhydride	2.25	++	++	++	++	++	–
Dimethyl fumarate	1.49	++	++	++	++	++	–
Divinylsulphone	1.33	++	+	+	+	+	–
Dimethyl maleate	1.27	++	++	+	–	–	–
Acrylonitrile	1.20	++	++	–	–	–	–

Note. ++) complex stable and can be isolated; +) a complex is formed but decomposes during isolation; –) no complex formed.

*tmeda = tetramethylethylenediamine.

The *e* values given in Table 4 are taken from Ref.66; they characterise the electronic properties of a grouping bonded to a vinyl radical. $e < 0$ for electron-donating, and $e > 0$ for electron-accepting substituents. Syrene (substituent = phenyl), for which $e = -1$, is used as a standard.

Stable complexes are formed only with olefins which have $e \geqslant 1.20$. Olefins with $e < 1.20$ [butyl acrylate (1.06), methacrylonitrile (0.81), acrylic acid (0.77), methyl vinyl ketone (0.68), and ethyl acrylate (0.22)] do not give stable olefinic complexes even when L = bipy; in all cases (bipy)Pd(DBA) compounds are formed. It also follows from Table 4 that stable complexes are formed with such good σ-donating and weak π-accepting ligands as bipy and phen; less powerful σ-donors, e.g. tmeda and $P(OR)_3$, form complexes only with a very strong π-acceptor, such as maleic anhydride. The weak σ-donor PPh_3 does not form stable mixed complexes with any of the olefins listed in Table 4; in all cases $Pd(PPh_3)_n$ is formed.

The reactions of olefins with Pt-complexes of DBA are similar[16,66] but as platinum is more nucleophilic than palladium[67] stable olefinic complexes are formed even with phosphines and arsines. The following complexes have been obtained:[39] $(PPh_3)_2Pt$(olefin) (where olefin = 4-phenylbut-3-en-2-one or 1,3-diphenylprop-2-en-1-one), $(PEt_3)_2Pt(CF_2=CF_2)$, and $(AsPh_3)_2Pt(CCl_2=CCl_2)$. Similar complexes are formed in the reaction of $L_2Pt(DBA)$ with olefins.[39] DBA is thus displaced from its complexes by an olefin such as tetrachloroethylene which is capable of displacing stilbene and diphenylacetylene from $(PPh_3)_2Pt$(olefin) complexes.[68,69] In the

sequence indicating the ease of substitution of ligands[60] DBA is placed next to acetylenes:

$$C_2H_4 < C_2H_2 \approx DBA < (CN)_2C{=}C(CN)_2 < (CO \approx PPh_3) < < O_2NC_6H_4C{\equiv}CC_6H_4NO_2.$$

p-Quinones react with $Pd_2(DBA)_3$ in the presence of neutral ligands similarly to olefins, forming L_2Pd(quinone) type complexes,[28] which can also be obtained by reactions of PdL_4 with the corresponding quinones.[70] However, the preparation of π-quinone complexes of palladium via the DBA complexes is more advantageous and gives products with a higher degree of purity and greater yields.

The reaction of olefins with DBA complexes of palladium in the presence of neutral ligands thus gives previously known[67] Pd^0 derivatives; their stability is governed by the delicate electronic balance between the donor and acceptor properties of the neutral ligands and the olefins. Quite recently, by combining electron-donating and electron-accepting olefins, a group of Japanese authors[71,72] has prepared mixed olefinic complexes of Pd^0 by the reaction of $Pd_2(DBA)_3$ with an electron-accepting olefin in the presence of an excess of an electron-donating olefin or diene. The acceptor olefins used were maleic anhydride, dimethyl fumarate, and tetracyanoethylene, and the donor olefins were cyclo-octadiene, norbornadiene, norbornene, and cyclopentene.

New tri-coordinated complexes of Pd^0 have been obtained by this method. Up to the present only two purely olefinic π-complexes of Pd^0 are known: $(cod)_2Pd$, where cod = cyclo-octa-1,5-diene,[73–76] and $(CH_2{=}CH_2)_3Pd$;[73–75] the method for preparing mixed olefinic derivatives proposed in Refs.71 and 72 offers further prospects for obtaining these practically important compounds. The stabilisation of Pd^0 by a combination of electron-donating and electron-accepting olefins evidently plays an important role in the palladium-catalysed cyclotrimerisation reactions between dimethyl acetylenedicarboxylate (an electron acceptor) and norbornadiene or norbornene (electron donors).[77]

(b) Reactions with acetylenes. Another very interesting aspect of the reactivity of DBA complexes of palladium and platinum is their reaction with acetylenes. The investigation of these reactions has provided many fundamentally important results which are of general significance for the chemistry of organometallic compounds of transition metals.

The ability of DBA complexes of palladium and platinum to react with alkynes has been mentioned in earlier work devoted mainly to the study of reactions with olefins.[16,20,39,64]

The reaction of $(PEt_3)_2Pt(DBA)$ with hexafluorobutyne in toluene at room temperature over a period of 48 h gives a quantitative yield of the known complex $(PEt_3)_2Pt(CF_3C{\equiv}CCF_3)$.[16] The same product is formed by the reaction of $(DBA)_2Pt$ with an excess of hexafluorobutyne in the presence of triethylphosphine[18,20] or of tetrakis(triethylphosphine)platinum with $CF_3C{\equiv}CCF_3$.[75]

The reaction of acetylenes with DBA derivatives of palladium has been studied more thoroughly. The reaction of $Pd_2(DBA)_3$ with dimethyl acetylenedicarboxylate (dmad) in the absence of phosphorus-containing or any other stabilising ligands leads to the formation of a polymeric cyclopentadiene-palladium complex which was isolated and characterised by its ^1H n.m.r. spectrum.[64]

A similar metalladiene complex of platinum, platinacyclopenta-2,4-diene, is formed by the reaction of dmad with $Pt(DBA)_2$ or $Pt(DBA)_3$.[76] It was not isolated pure but was characterised by the ^1H n.m.r. spectrum and by conversion to the bis(triphenylphosphine) adduct $\{(PPh_3)_2Pt[C(COOMe)]_4\}_n$. These metallacyclopentadiene complexes are suggested to be intermediates in the cyclotrimerisation of acetylenes catalysed by Pd^0 and Pt^0 compounds.[76]

The results of the reaction of $Pd_2(DBA)_3$ with dmad in the presence of *n*-donor ligands depend to a considerable extent on the nature of the ligand used.[64,77] In the case of PPh_3 a bis(triphenylphosphine) complex of Pd^0 with dmad is formed initially; this complex reacts with a second dmad molecule to form palladiacyclopentadiene. $P(OPh)_3$ also reacts with $Pd_2(DBA)_3$ and dmad to give bis(triphenylphosphite)(dmad)palladium(0) in the initial stage but the latter complex is not converted to palladiacyclopentadiene on reaction with excess of the alkyne. However, treatment of the polymeric palladiacyclopentadiene with triphenyl phosphite gives bis(triphenylphosphite)palladiacyclopentadiene as expected. Bidentate *n*-donor ligands (bipy, phen, tmeda, dmg, bte, badn)† react with $Pd_2(DBA)_3$ in the presence of dmad, by-passing the π-acetylene complex stage, and forming the corresponding palladiacyclopentadiene straightaway. It is interesting in this regard that the reaction between bipy, $Pd_2(DBA)_3$, and maleic anhydride takes place with intermediate formation of a π-olefinic complex which is later converted to palladiacyclopentadiene. The stability of the intermediate π-acetylene complex therefore depends on the nature of the *n*-donor ligand, as follows: bipy ≈ phen ≪ PPh_3 < $P(OPh)_3$. In this sequence from left to right there is a marked increase in the π-accepting ability of the ligands which will stabilise the π-acetylenic derivatives of Pd^0.[78]

The palladium complex of TBAA referred to previously reacts with dmad in the presence of bipy to form the bipyridyl complex of palladiacyclopentadiene.[39]

(c) Preparation of enyl type complexes. The ability of DBA derivatives of Pd to form π-allyl complexes by oxidative addition of allyl substrates, which was mentioned in the early work of Japanese authors,[1] is a characteristic property of Pd^0 compounds. μ-Bridging bis-π-allylpalladium halides or cationic π-allyl complexes can be obtained depending on the way the reaction is carried out. For example, the reaction of $Pd_2(DBA)_3$ with methylallyl chloride in benzene gives di-μ-chloro-bis(π-methylallylpalladium);[1] allyl bromide, allyl chloride, but-2-enyl chloride, and cinnamyl chloride react similarly. The rate of oxidative addition varies in the order:[64]

$$C_3H_5Br > C_3H_5Cl > 2\text{-}C_4H_7Cl > 1\text{-}C_4H_7Cl > 3\text{-}PhC_3H_4Cl.$$

For example, the reaction with allyl chloride takes 5 min but with cinnamyl chloride 30 min are required.

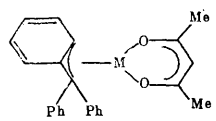
If the complex (bipy)Pd(DBA) is used in the reaction with the allyl halides or $Pd(DBA)_2$ is used in the presence of bipy, then cationic π-allyl complexes of palladium are formed.[64] The reactions of the allyl halides with the complex $(TBAA)_3Pd_3.CHCl_3$ are similar.[39] However, all these reactions are of no practical interest for the preparation of π-allyl complexes of palladium. Unfortunately π-allyl halide compounds of platinum, which are difficult to obtain, cannot be produced by this method. The reaction of DBA complexes of Pt with allyl halides takes place in the presence of donor ligands and gives cationic π-allyl compounds of platinum which are of little interest from a practical point of view.

Allyloxyphosphonium and allylisothiouronium salts react with $Pd_2(DBA)_3$ in a similar way to the allyl halides; in the presence of donor ligands cationic π-allyl complexes of palladium are formed in high yields.[79]

‡dmg = dimethylglyoxime, bte = 1,2-bis(methylthio)ethane, and badn = biacetyldianil.

In all the work quoted above in this section[1,39,64,79] the π-allyl complexes are formed from compounds which already contain an allylic system (allyl halides, allyloxyamidophosphonates, allylisothiouronium salts, etc.), so that the production of π-allylic compounds is not unexpected. On the contrary, in view of the clear tendency of palladium to form π-allylic type complexes,[80] the isolation of π-allylic derivatives from these reactions is a normal result.

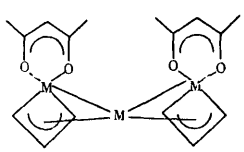
From this point of view the series of papers on the reaction of DBA complexes of palladium and platinum with triphenylmethyl chloride[81-83] and triarylcyclopropenylium bromide[84-86] form a clear contrast. Although the benzyl group is known to be capable of η^3-type bonding with a transition metal atom,[87-92] the formation of a π-allylic ligand from triphenylmethyl precursors has not been established with a sufficient degree of certainty.[93] Complexes of the $\{M[CPh_2(C_6H_4X)]Cl\}_n$ (M = Pd, Pt; X = H, F, OMe) type have been obtained by the reaction of dibenzylideneacetone derivatives of palladium or platinum with substituted triphenylchloromethanes.[82] For these compounds a dimeric structure with a Pd_2Cl_2 bridging fragment was proposed on the basis of the far infrared spectra [ν(M−Cl) = 288 cm^{-1}] and molecular weight determination. X-Ray structure determinations on acetylacetonate derivatives[83] showed that the Pd and Pt compounds are isostructural and there is η^3-coordination of the CPh_3-ligand with the metal atom, i.e. the structure of the complex in the crystalline state is:



M = Pd, Pt

The importance of this work[81-83] is that the results obtained enable the structure of similar nickel complexes, which were prepared as long ago as 1966,[93] to be described correctly.

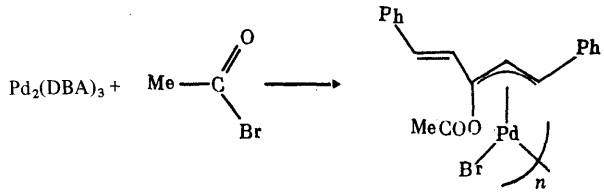
Interesting structure types of η^3-complexes have been reported.[84-86] The reaction of DBA complexes of palladium and platinum with phenyl-substituted cyclopropenylium bromides gives sparingly soluble complexes of the $[M_3(C_3R^1R^2_2)_2Br]$ type which undergo reactions that are typical of complexes with bridging M_2Cl_2 fragments.[86] An X-ray structure determination was carried out on $Pd_3[C_3Ph(p\text{-}MeOC_6H_4)_2]_2(acac)_2$. The structure[85] can be described as two palladiacyclobutenyl "units" $\{(acac)Pd(C_3R^1R^2_2)\}$, with η^3-type bonding of each of them to a third palladium atom:



M = Pd

Thus during the reaction a C−C bond in the cyclopropenyl ring has been broken; in the unsymmetrically substituted phenyldi-(4-methoxyphenyl)cyclopropenylium bromide it is predominantly the $MeOC_6H_4C-CC_6H_4OMe$ bond that is broken.

Another unusual η^3-complex has been obtained by the reaction of $Pd_2(DBA)_3$ with acetyl bromide:[94]



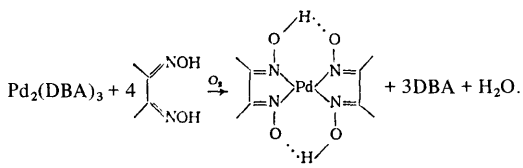
Treatment of this complex with aqueous NaOH regenerates the original $Pd_2(DBA)_3$, reactions with thallium β-diketonates or cyclo-octa-1,5-diene in the presence of $AgPF_6$ lead to cleavage of the μ-bromide bridges and formation of monomeric [(PhCH=CHC(OCOMe)C_2H_2Ph)Pd(acac)] or {[PhCH=CHC(OCOMe).C_2H_2Ph]Pd(cod)]PF_6.

The formation of a π-allylic ligand can be represented as attack by $MeCO^+$ on the oxygen atom of the carbonyl group in DBA; a similar process—the formation of allylic complexes of iron by the reaction of $MeCO^+BF_4^-$ with $Fe[RCH=CHC(O)R^1](CO)_4$—has been reported.[95]

2. Other Reactions of DBA Complexes of Palladium and Platinum

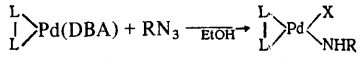
Some of the reactions discussed in this section have been mentioned previously. For example, the total replacement of DBA by phosphines,[16,28] and partial substitution by bipyridyl and phenanthroline[18,21] and also by phosphines and arsines.[16] Below we shall consider reactions of DBA derivatives, mainly those of palladium, which also take place with total or partial replacement of the DBA and lead to the formation of various palladium complexes which are, in a number of instances, difficult or impossible to prepare by other methods. A common feature of the reactions discussed below is oxidation of the metal atom (particularly palladium to form Pd^{II} derivatives), i.e. these processes are essentially reactions in which there is oxidative addition to a complex of palladium in a low-valent state. However, the special properties of DBA complexes lead, in this instance, to unexpected results. For example, the oxidation of triphenylphosphine complexes of zerovalent nickel, palladium, and platinum by oxygen is known to give peroxo-deriva-tives of these metals.[96] The dibenzylideneacetone derivative of palladium does not form peroxo-complexes under these conditions; the oxidation of $Pd_2(DBA)_3$ by oxygen in the presence of bipy gives (bipyridyl)dihydroxopalladium[18,64] and formaldehyde. The forma-tion of formaldehyde in this reaction presupposes the intermediate formation of (bipyridyl)peroxopalladium which is reduced by methanol to the dihydroxo-complex. It is interesting that oxidation of (bipy)Pd(DBA) by the action of 7% H_2O_2 in methanol also gives (bipyridyl)dihydroxopalladium.[64]

The oxidation of $Pd_2(DBA)_3$ by oxygen in the presence of dimethylglyoxime takes place quite differently:[18,64]



All the oxygen is quantitatively used in converting the oxime hydrogen to water; similar reactions are observed with acetylacetone and 8-quinolinol.[64]

In the reaction of (L−L)Pd(DBA), where L−L = bipy or phen, with aroyl- or tosyl azides the DBA ligand is displaced and amide derivatives of palladium(II) are formed:[97]



R=4-MeC$_6$H$_4$CO, X=N$_3$, L—L=bipy;
R=Ts, X=NHTs, L—L=bipy;
R=Ts, X=NHTs, L—L=phen.

(L—L)Pd(N$_3$)$_2$ type complexes, which were identified by i.r. spectroscopy, are formed as by-products. If the reaction is carried out in methanol instead of ethanol the amount of by-product increases.

Table 5. Use of dibenzylideneacetone complexes of palladium as catalysts.

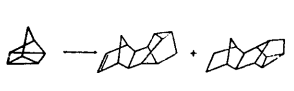
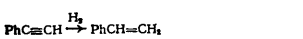
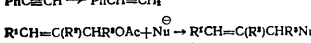
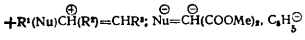
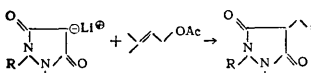
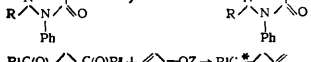
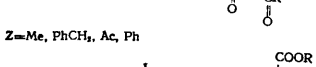
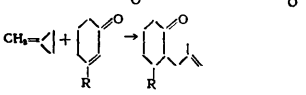
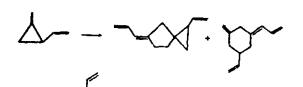
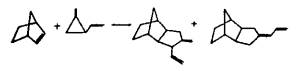
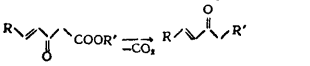
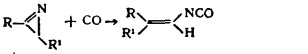
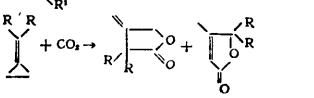
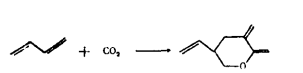
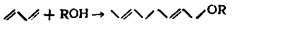
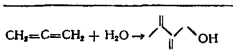
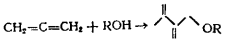
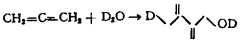
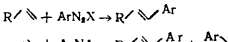
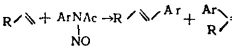
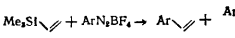
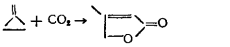
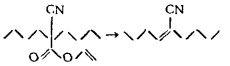
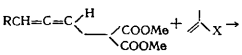
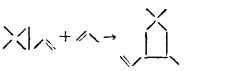
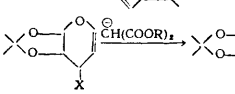
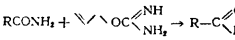
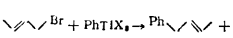
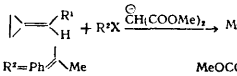
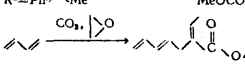
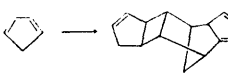
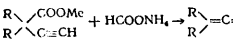
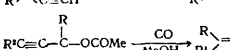
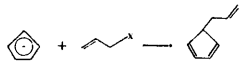
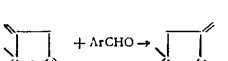
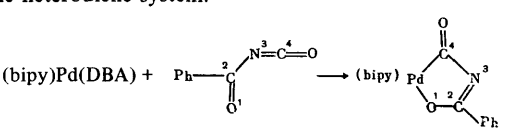
Reaction	Catalyst	Refs.
	Pd$_2$(DBA)$_3$.CHCl$_3$	[118]
	Pd$_2$(DBA)$_3$.PhC≡CH	[119, 120]
	Pd(DBA)$_2$.DPPE	[121]
	Pd$_2$(DBA)$_3$.DPPE	[122]
	Pd$_2$(DBA)$_3$	[123]
	Pd(DBA)$_2$.DIOP	[124]
	Pd$_2$(DBA)$_3$.CHCl$_3$.L L = PPh$_3$, DPPE	[125]
	Pd$_2$(DBA)$_3$.CHCl$_3$	[126]
	Pd(DBA)$_2$.PR$_3$	[127]
	Pd(DBA)$_2$.PR$_3$	[127]
PhCH(Me)Br → PhCH(Me)CH(Me)Ph	R$_4$N[Pd(OH)DBA$_2$]	[128]
ArCH$_2$X + CO → ArMe + ArCH$_2$CH$_2$Ar	Pd(DBA)$_2$	[129]
	Pd$_2$(DBA)$_3$.PR$_3$	[130]
H$_2$ + O$_2$ → H$_2$O$_2$	Pd(DBA)$_3$	[131]
	Pd(DBA)$_2$	[132]
	Pd(DBA)$_2$.PR$_3$	[133]
	Pd$_2$(DBA)$_3$	[134]
RhCH=CH$_2$ + CO + MeOH → PhCHCOOMe (Me)	Pd$_2$(DBA)$_3$	[135]
	Pd$_2$(DBA)$_3$	[136]

Table 5 (contd.).

Reaction	Catalyst	Refs.
	Pd(DBA)$_2$.PR$_3$	[137]
	Pd(DBA)$_2$.PR$_3$	[137]
	Pd(DBA)$_2$.PR$_3$	[137]
	Pd(DBA)$_2$	[138—140]
	Pd(DBA)$_2$	[141]
	Pd(DBA)$_2$.MeCN	[142]
ArCl + R$_6$Si$_2$ → ArSiR$_3$	Pd$_2$(DBA)$_3$	[143, 144]
	Pd(DBA)$_2$.PPh$_3$	[145]
	Pd$_2$(DBA)$_3$.CHCl$_3$.PPh$_3$	[146]
	Pd(DBA)$_2$.DPPE	[147]
	Pd$_2$(DBA)$_3$.CHCl$_3$.PR$_3$	[148]
	Pd(DBA)$_2$.DPPE	[149]
	Pd(DBA)$_2$.DPPE	[150]
	Pb$_2$(DBA)$_3$	[151]
	Pd$_2$(DBA)$_3$.diphos	[152]
	Pd$_2$(DBA)$_3$	[153]
	Pd$_2$(DBA)$_3$	[154]
	Pd$_2$(DBA)$_3$.PR$_3$	[155]
	Pd$_2$(DBA)$_3$.PPh$_3$	[156]
	Pd$_2$(DBA)$_3$	[157]
	Pd$_2$(DBA)$_3$	[158]
	Pd$_2$(DBA)$_3$.PBu$_3$	[159]

Benzoyl isocyanate reacts with (bipy)Pd(DBA) by a completely different route, forming a metallaoxazoline ring by 1,4-addition of Pd^0 to the heterodiene system:[98]

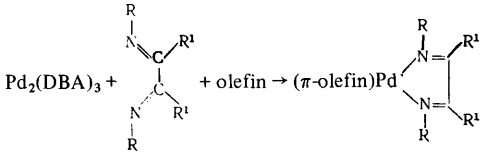


A similar palladiathiazoline complex is formed by the reaction of (bipy)Pd(DBA) with thiobenzoyl isocyanate.[98] The same compound is obtained in a quantitative yield by the reaction of (bipy)Pd(DBA) with 2-phenylthiazoline-4,5-dione.[98] During the reaction CO is liberated vigorously; it is assumed[98] that a palladiathiazine derivative is formed initially and this is converted to the palladiathiazoline complex with elimination of carbon monoxide. However, under the same conditions the biacetylanil derivative of dibenzylideneacetonepalladium reacts with phenylthiazoline-4,5-dione without elimination of CO, giving a 76% yield of the palladiathiazoline complex. This complex does not eliminate CO even on heating.

The use of dibenzylideneacetone complexes to obtain various σ-derivatives of palladium and platinum is described in a series of papers.[100–106]§ σ-phenyl complexes of palladium with sterically hindered phenoxy groups have been synthesised by the Reutov–Sokolov method (see Ref.108); the preparation of σ-palladiated complexes by using $Pd(DBA)_3$ has been reported.[109–115]

In all the reactions listed above in this section there is oxidative addition of the various substrates to Pd^0 with formation of Pd^{II} derivatives. There are two reports in which DBA compounds of Pd^0 react either without a change in the formal oxidation state of the palladium[114] or with the formation of formally univalent palladium derivatives.[115]

In Ref.114 complexes of palladium with 1,4-diazabutadienes were obtained starting from $Pd_2(DBA)_3$, $Pd_3(TBAA)_3$, and $Pd_3(TTAA)_3$ (TTAA = tritoluylideneacetylacetone) which was synthesised by the authors. However, the anticipated (1,4-diazabutadiene)Pd(DBA) type complexes could not be isolated because they are too unstable. In the opinion of these authors[114] the reason for the instability of such compounds is the imbalance between the electron-donating and electron-accepting properties of 1,4-diazabutadiene and DBA. Whereas the former is a strong σ-donor, the π-accepting properties of DBA are clearly insufficient to reduce the electron density on the metal atom. To stabilise the complexes it is necessary to use either less basic diazabutadienes or ligands which are better π-acceptors than dibenzylideneacetone. Hence the principles governing the choice of ligand will be approximately the same as in the preparation of π-olefinic complexes of Pd^0 starting from $Pd_2(DBA)_3$ (see above). In fact, the introduction of strongly electron-accepting substituents into the 1,4-diphenyldiazabutadiene molecule led to the formation of a stable Pd^0 compound. On the other hand, the use of electron-accepting olefins [tetracyanoethylene (TCNE), maleic anhydride (MA), dimethyl fumarate (DMF), and diethyl fumarate (DEF)] as co-reagents enables olefin-diazabutadiene complexes of Pd^0 with more basic diazabutadienes to be obtained:



R = Bu^t, R^1 = H, olefin = TCNE; R = Bu^t, R^1 = H, olefin = MA; R = Pr^i, R^1 = H, olefin = MA; R = cyclo-C_6H_{11}, R^1 = H, olefin = MA; R = cyclo-C_3H_5, R^1 = Me, olefin = DMF; R = 4-$MeOC_6H_4$, R^1 = H, olefin = DMF; R = 4-$MeOC_6H_4$, R^1 = H, olefin = DEF; R = Bu^t, R^1 = H, olefin = DMF; R = Bu^t, R^1 = H, olefin = DEF; R = Pr^i_2CH, R^1 = H, olefin = DMF.

§For more detail see the review in Ref.107.

A comparison of these results with those in Table 4 shows that all the diazabutadienes used have σ-donor properties which surpass those of such strong σ-donors as trimethyl and triphenyl phosphite and resemble those of tetramethylethylenediamine.

The reaction of $Pd_2(DBA)_3$ with an excess of MeNC gives solutions which are stable in the absence of air and which react with iodine to give the Pd^{II} derivative $(MeNC)_2PdI_2$. The $Pd_2(DBA)_3$/MeNC system is concluded to be a synthetic equivalent of $Pd(MeNC)_x$ species. The reaction of $Pd_2(DBA)_3$ and methyl isocyanide with $[(MeNC)_4Pd](PF_6)_2$ gives dimeric Pd^I complexes in a good yield.[115]

Similar dimers containing Pd–Pd, Pd–Pt, and Pd–Mn bonds have been obtained.[116,117]

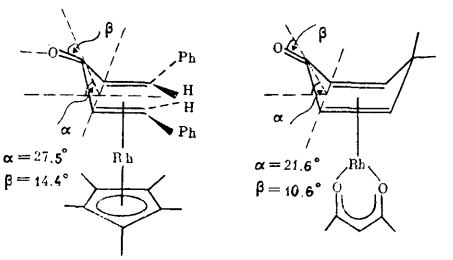
VI. USE OF DBA COMPLEXES OF THE PLATINUM METALS AS HOMOGENEOUS CATALYSTS

DBA complexes, particularly those of palladium, have recently been intensively studied as catalysts of very varied reactions. An attempt to classify this work is made in Table 5.

It appears from the examples given in this table that catalysis by DBA complexes of palladium in essence differs little from catalysis by other Pd^0 complexes[160,161] but the use of DBA catalysts is to be preferred because of their easy accessibility and the simplicity of working with them.

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The bulk of the work on the chemistry of DBA complexes of transition metals and determination of their structures was carried out in the period 1971–1974 and subsequent publications relate mainly to their use as reagents, catalysts, etc. DBA derivatives of palladium and platinum are now firmly established in preparative organometallic chemistry as highly reactive starting materials suitable for the synthesis of the most diverse classes of organo-Pd and organo-Pt compounds. However, the DBA molecule may be of interest in organometallic chemistry not only as an olefinic or dienone ligand as such but also as a model structural fragment in a number of more complex organic molecules of other classes. For example, metal complexes with semi-quinonoid π-ligands can be regarded[162] as unusual "closed" analogues of DBA complexes like $(DBA)RhC_5Me_5$,[26] as follows:



The validity of this analogy is confirmed by the considerable similarity observed in the angles α and β, which characterise the conformational changes in the dienone system resulting from π-coordination of the double bonds to the transition metal atom.[162]

REFERENCES

1. Y.Takahashi, Ts.Ito, S.Sakai, and Y.Ishii, Chem. Communs., 1970, 1065.
2. K.Moseley and P.M.Maitlis, Chem. Communs., 1971, 982.
3. E.Koerner von Gustorf, F.W.Grevels, C.Krüger, et al., Z.Naturforsch., 1972, **276b**, 392.
4. R.G.Iarr and R.J.Parizer, Chem. Phys., 1955, **23**, 711.
5. J.N.Murrell, "The Theory of the Electronic Spectra of Organic Molecules", Methuen, London; Wiley, New York, 1963.
6. E.Paspaleev and A.Kojucharova, Monatsh. Chem., 1969, **100**, 1213.
7. E.Koerner von Gustorf, M.C.Henry, and D.J.McAdoo, Annalen, 1967, **707**, 190.
8. M.Herberhold, "Metal π-Complexes. Complexes with Mono-olefin Ligands" (Translated into Russian), Mir, Moscow, 1975, p.273.
9. B.A.Arbuzov, L.K.Yuldasheva, I.V.Anonimova, et al., Izv. Akad. Nauk SSSR, Ser. Khim., 1969, 1485.
10. T.Hoshi, T.Kawashima, J.Okubo, et al., J. Chem. Soc. Perkin Trans.II, 1986, 1147.
11. R.Bramley and R.J.Le Fevre, J. Chem. Soc., 1962, 56.
12. L.M.Kataeva, E.G.Kataev, and T.G.Monnafarov, Zhur. Strukt. Khim., 1966, **7**, 226.
13. B.A.Arbuzov, L.K.Yuldasheva, I.V.Anonimova, et al., Izv. Akad. Nauk SSSR, Ser. Khim., 1969, 1258.
14. H.Tanaka, K.Yamada, and H.Kawazura, J. Chem. Soc. Perekin Trans.II, 1978, 231.
15. J.B.Bentley, K.B.Everard, R.J.B.Maraden, and L.E.Sutton, J. Chem. Soc., 1949, 2957.
16. W.J.Cherwinski, B.F.G.Johnson, and J.Lewis, J. Chem. Soc. Dalton Trans., 1974, 1405.
17. B.F.G.Johnson, J.Lewis, G.R.Stephenson, and E.J.S.Vichi, J. Chem. Soc. Dalton Trans., 1978, 369.
18. Y.Ishii, Ann. New York Acad. Sci., 1974, **239**, 114.
19. B.E.Mann, A.Sonoda, and O.M.Maitlis, quoted in J. Chem. Soc. Dalton Trans., 1974, 169.
20. W.J.Cherwinski, B.F.G.Johnson, and J.Lewis, J. Organometal. Chem., 1973, **52**, C61.
21. T.U.Ykai, H.Kawazura, and Y.Ishii, J. Organometal. Chem., 1974, **65**, 253.
22. N.W.Alcock, N.Herron, T.J.Kemp, and C.W.Shoppee, Chem. Communs., 1975, 785.
23. N.W.Alcock, P.Meester, and T.J.Komp, J. Chem. Soc. Perkin Trans.II, 1979, 921.
24. N.W.Alcock and P.Meester, Acta Cryst., 1979, **35**, 609.
25. H.B.Lee and P.M.Maitlis, J. Organometal. Chem., 1973, **57**, C87.
26. J.A.Ibers and P.M.Maitlis, J. Organometal. Chem., 1974, **73**, 389.
27. M.C.Mazza and C.G.Pierpont, Inorg. Chem., 1973, **12**, 2955.
28. M.C.Mazza and C.G.Pierpont, Chem. Communs., 1973, 207.
29. C.G.Pierpont and M.C.Mazza, Inorg. Chem., 1974, **13**, 1891.
30. C.G.Pierpont, R.M.Buchanan, and H.H.Downs, J. Organometal. Chem., 1977, **124**, 103.
31. H.Kawazura, H.Tanaka, K.Yamada, et al., Bull. Chem. Soc. Japan, 1978, **51**, 3466.
32. H.Tanaka and H.Kawazura, Bull. Chem. Soc. Japan, 1979, **52**, 2815.
33. H.Tanaka and H.Kawazura, Bull. Chem. Soc. Japan, 1980, **53**, 1743.
34. N.Rosch and R.Hoffmann, Inorg. Chem., 1974, **13**, 2656.
35. L.Malatesta and M.Angoletta, J. Chem. Soc., 1957, 1186.
36. A.Keasey, B.E.Mann, A.Yates, and P.M.Maitlis, J. Organometal. Chem., 1978, **152**, 117.
37. K.Moseley and P.M.Maitlis, J. Chem. Soc. Dalton Trans., 1974, 169.
38. M.C.Mazza and C.G.Pierpont, Inorg. Chem., 1973, **12**, 2955.
39. Y.Ishii, S.Hasegawa, S.Kimura, and K.Itoh, J. Organometal. Chem., 1974, **73**, 411.
40. J.A.S.Howell, B.F.G.Johnson, and P.L.Josly, J. Organometal. Chem., 1972, **39**, 329.
41. D.H.R.Barton, A.A.L.Gunalilaka, T.Makanishi, et al., J. Chem. Soc. Perkin Trans.I, 1976, 821.
42. G.Scholes, C.R.Graham, and M.Brookhart, J. Amer. Chem. Soc., 1974, **96**, 5665.
43. J.A.Paquette, J.M.Photis, and G.D.Ewing, J. Amer. Chem. Soc., 1975, **97**, 3358.
44. M.Brookhard, G.O.Nelson, G.Scholes, and R.A.Watson, Chem. Communs., 1976, 195.
45. G.Cardacci and G.Concetti, J. Organometal. Chem., 1975, **90**, 49.
46. A.Vessieres and P.Dixneuf, Tetahedron Lett., 1974, 1499.
47. A.Vessieres and P.Dixneuf, J. Organometal. Chem., 1976, **108**, C5.
48. R.D.Gillard, B.T.Heaton, and M.F.Pilbrow, J. Chem. Soc.A, 1970, 353.
49. B.T.Heaton and D.J.A.McCaffrey, J. Organometal. Chem., 1972, **43**, 437.
50. G.W.Parshall and G.Wilkinson, Inorg. Chem., 1962, **4**, 987.
51. C.W.Fong and W.Kitching, Austral. J. Chem., 1969, **22**, 477.
52. P.Practorius and F.Korn, Ber., 1910, **43**, 2744.
53. H.Stobbe and E.Färber, Ber., 1925, **58**, 1548.
54. C.W.Shoppee, Y.-S.Wang, S.Sternhell, and G.C.Brophy, J. Chem. Soc. Perkin Trans.I, 1976, 1880.
55. C.W.Shoppee and G.N.Henderson, Chem. Communs., 1974, 561.
56. A.Z.Rubezhov, Tetrahedron Lett., 1977, 2189.
57. M.Boyer, Compt. rend., 1966, **263**, 1072.
58. P.F.Gasals, Bull. Soc. chim. France, 1963, 253.
59. P.F.Gasals, Bull. Soc. chim. France, 1963, 264.
60. A.Z.Rubezhov and S.P.Gubin, Adv. Organometal. Chem., 1972, **10**, 347.
61. S.J.Ashcroft, A.Maddock, and G. Beech, J. Chem. Soc. Dalton Trans., 1974, 462.
62. M.Herberhold, "Metal π-Complexes. Complexes with Mono-olefin Ligands" (Translated into Russian), Mir, Moscow, 1975, p.136.
63. Ts.Ito, Y.Takahashi, and Y.Ishii, Chem. Communs., 1972, 629.
64. Ts.Ito, S.Hasegawa, Y.Takahashi, and Y.Ishii, J. Organometal. Chem., 1974, **73**, 401.
65. J.Tsuji, J. Organometal. Chem., 1986, **300**, 281.
66. J.B.Randrup and E.H.Immergut, Polymer Handbook, Intersci., New York, 1966, p.11.
67. P.M.Maitlis, "The Organic Chemistry of Palladium", Vol.1, Acad. Press, New York–London, 1971.
68. W.J.Bland and R.D.W.Kemmitt, J. Chem. Soc.A, 1968, 1278.
69. C.D.Cook and K.Y.Wang, Inorg. Chem., 1971, **13**, 2696.
70. S.Takahashi and N.Hagihara, J. Chem. Soc. Japan (Pure Chem. Sect.), 1967, **88**, 1306.
71. K.Itoh, F.Ueda, and Y.Ishii, Intern.Conf. Organometal. Chem., Kyoto, 1977, 4AO7, 62.

72. K.Itoh, F.Ueda, K.Hirai, and Y.Ishii, Chem. Lett., 1977, 877.
73. M.Green, J.A.K.Howard, J.L.Spencer, and F.G.A.Stone, Chem. Communs., 1975, 3.
74. M.Green, J.A.K.Howard, J.L.Spencer, and F.G.A.Stone, Chem. Communs., 1975, 449.
75. M.A.Bennet, G.B.Robertson, P.O.Whip, and T.Yoshida, J. Amer. Chem. Soc., 1971, **93**, 3797.
76. K.Moseley and P.M.Maitlis, Chem. Communs., 1971, 1604.
77. Ts.Ito, S.Hasegawa, Y.Takahashi, and Y.Ishii, Chem. Communs., 1972, 629.
78. A.Z.Rubezhov, "Metody Elementoorganicheskoi Khimii. Kobal't, Nikel', Platinovye Metally" (Methods in Hetero-organic Chemistry. Cobalt, Nickel, and the Platinum Metals), Nauka, Moscow, 1978, p.566.
79. P.Grenoillet, D.Neibecker, and I.Tkatchenko, Inorg. Chem., 1980, **19**, 3189.
80. A.Z.Rubezhov, Thesis for the Degree of Candidate of Chemical Sciences, Institute of Hetero-organic Compounds, Academy of Sciences of the USSR, Moscow, 1967.
81. A.Sonoda, B.E.Mann, and P.M.Maitlis, Chem. Communs., 1975, 208.
82. B.E.Mann, A.Keasey, A.Sonoda, and P.M.Maitlis, J. Chem. Soc. Dalton Trans., 1979, 338.
83. A.Sonoda, P.M.Bailey, and P.M.Maitlis, J. Chem. Soc. Dalton Trans., 1979, 346.
84. A.Keasley, P.M.Bailey, and P.M.Maitlis, Chem. Communs., 1977, 178.
85. P.M.Bailey, A.Keasey, and P.M.Maitlis, J. Chem. Soc. Dalton Trans., 1978, 1825.
86. A.Keasey and P.M.Maitlis, J. Chem. Soc. Dalton Trans., 1978, 1830.
87. R.B.King and A.Fronzaglia, J. Amer. Chem. Soc., 1966, **88**, 709.
88. F.A.Cotton and M.D.Laprade, J. Amer. Chem. Soc., 1968, **90**, 5418.
89. F.A.Cotton and T.J.Marks, J. Amer. Chem. Soc., 1969, **91**, 1339.
90. R.R.Stevens and G.D.Shier, J. Organometal. Chem., 1970, **21**, 495.
91. J.S.Roberts and K.J.Klabunde, J. Amer. Chem. Soc., 1977, **99**, 2509.
92. E.L.Muetterties and F.J.Hirsekorn, J. Amer. Chem. Soc., 1974, **96**, 7920.
93. G.Wilke and H. Schott, Angew. Chem. Int. Ed. Engl., 1966, **5**, 583.
94. A.Sonoda, B.E.Mann, and P.M.Maitlis, J. Organometal. Chem., 1975, **96**, C16.
95. A.N.Nesmeyanov, L.V.Rybin, N.T.Gubenko, et al., J. Organometal. Chem., 1974, **71**, 271.
96. S.Otsuka, A.Nakamura, and T.Tatsuno, J. Amer. Chem. Soc., 1969, **91**, 6994.
97. S.Cenin, M.Pizzotti, F.Porta, and G.La Monica, J. Organometal. Chem., 1975, **88**, 237.
98. S.Hasegawa, K.Itoh, and Y.Ishii, Inorg. Chem., 1974, **13**, 2675.
99. V.I.Sokolov, V.V.Bashilov, and O.A.Reutov, J. Organometal. Chem., 1975, **97**, 299.
100. L.L.Troitskaya, A.I.Grandberg, V.I.Sokolov, and O.A.Reutov, Dokl. Akad. Nauk SSSR, 1876, **228**, 367.
101. V.I.Sokolov, V.V.Bashilov, and O.A.Reutov, J. Organometal. Chem., 1976, **111**, C13.
102. V.I.Sokolov, L.L.Troitskaya, and O.A.Reutov, J. Organometal. Chem., 1975, **93**, C11.
103. V.I.Sokolov, V.V.Bashilov, A.A.Musaev, and O.A.Reutov, J. Organometal. Chem., 1982, **225**, 57.
104. V.V.Bashilov, E.V.Maskaeva, A.A.Musaev, et al., Izv. Akad. Nauk SSSR, Ser. Khim., 1984, 1597.
105. L.L.Troitskaya, V.I.Sokolov, and O.A.Reutov, Dokl. Akad. Nauk SSSR, 1977, **236**, 371.
106. V.V.Bashilov, E.V.Maskaeva, P.V.Petrovskii, and V.I.Sokolov, J. Organometal. Chem., 1985, **292**, 89.
107. V.V.Bashilov, V.I.Sokolov, and O.A.Reutov, Izv. Akad. Nauk SSSR, Ser. Khim., 1982, 2069.
108. E.R.Milaeva, A.Z.Rubezhov, A.I.Prokofiev, et al., J. Organometal. Chem., 1980, **188**, C43.
109. P.W.Clark and S.F.Dyke, J. Organometal. Chem., 1985, **281**, 389.
110. P.W.Clark and S.F.Dyke, J. Organometal. Chem., 1984, **276**, 421.
111. H.-P.Abicht, J. Organometal. Chem., 1986, **311**, 57.
112. R.McCrindle, D.K.Stephenson, A.J.McAlecs, and J.M.Wilson, J. Chem. Soc. Dalton Trans., 1986, 641.
113. S.Park, D.Hedden, A.L.Rheingold, and D.M.Roundhill, Organometallics, 1986, **5**, 1305.
114. K.J.Covell, D.J.Stufkens, and K.Vrieze, Inorg. Chim. Acta, 1980, **47**, 67.
115. J.R.Boehm, D.J.Doonan, and A.L.Balch, J. Amer. Chem. Soc., 1976, **98**, 4845.
116. P.Espinet, J.Fornies, C.Fortuno, et al., J. Organometal. Chem., 1986, **317**, 105.
117. B.F.Hoskins, R.J.Steen, and T.W.Turney, J. Chem. Soc. Dalton Trans., 1984, 1831.
118. R.I.Khusnutdinov, V.A.Dokichev, I.O.Popova, et al., Izv. Akad. Nauk SSSR, Ser. Khim., 1985, 475.
119. A.I.Min'kov, N.K.Eremenko, O.A.Efimov, and A.N.Ponomarenko, USSR P.932 692; Byull. Izobr., 1983(28).
120. A.I.Min'kov, O.A.Efimov, O.V.Kapshutar', and N.K.Eremenko, Kinetika i Kataliz, 1984, **25**, 1090.
121. J.C.Fiaud and J.L.Malleron, Tetrahedron Lett., 1980, **21**, 4437.
122. J.C.Fiaud and J.L.Malleron, Chem. Communs., 1981, 1159.
123. B.P.2 108 125; Organometal. Comp., 1983, **43**, 339.
124. J.C.Fiaud, A.Hibon de Gournay, M.Zarcheveque, and H.B.Kogan, J. Organometal. Chem., 1978, **154**, 175.
125. J.Tsuji, I.Shimizu, I.Minami, and Y.Ohashi, Tetrahedron Lett., 1982, **23**, 4809.
126. G.Balavoine, C.Eskenazi, and M.Guillemot, Chem. Communs., 1979, 1109.
127. P.Binger and A.Germer, Chem. Ber., 1981, **114**, 3325.
128. V.Galomb and H.Alper, Chem. Communs., 1983, 88.
129. H.Alper, K.Hashem, and J.Heveling, Organometallics, 1982, **1**, 775.
130. European P.133 548; Organometal. Comp., 1985, **46**(2660).
131. US P.4 347 232; Organometal. Comp., 1982, **41**(3643).
132. H.Alper and C.P.Mahatantila, Organometallics, 1982, **1**, 70.
133. Y.Inoue, T.Hibi, M.Satake, and H.Hashimoto, Chem. Communs., 1979, 982.
134. BRD P.3 317 013; Organometal. Comp., 1985, **46**(368).
135. European P.74 866 (1983); Organometal. Comp., 1983, **42**(3278).
136. French P.2 459 075 (1981); Organometal. Comp., 1981, **39**(1025).

137. Y.Inoue, Y.Ohtsuka, and H.Hashimoto, Bull. Chem. Soc. Japan, 1984, **57**, 3345.
138. K.Kikukawa and T.Matsuda, Chem. Lett., 1977, 159.
139. K.Kikukawa, K.Nagira, N.Terao, et al., Bull. Chem. Soc. Japan, 1979, **52**, 2609.
140. K.Kikukawa, K.Nagira, F.Wada, and T.Matsuda, Tetrahedron, 1981, **37**, 31.
141. K.Kikukawa, N.Naritomi, G.-X.He, et al., J. Org. Chem., 1985, **50**, 299.
142. K.Kikukawa, K.Ikenaga, K.Nono, et al., J. Organometal. Chem., 1984, **270**, 277.
143. European P.57 858; Organometal. Comp., 1982, **41**(2324).
144. US P.4 363 925; Organometal. Comp., 1983, **42**(1931).
145. BRD P.3 403 793; Organometal. Comp., 1985, **47**(2625).
146. I.Minami, M.Yuhara, I.Shimizu, and J.Tsuji, Chem. Communs., 1986, 118.
147. M.Ahmar, B.Cazes, and J.Gore, Tetrahedron Lett., 1985, **26**, 3795.
148. I.Shimizu, Y.Ohashi, and J.Tsuji, Tetrahedron Lett., 1985, **26**, 3825.
149. T.V.RajanBabu, J. Org. Chem., 1985, **50**, 3642.
150. Y.Inoue, M.Taguchi, and H.Hashimoto, Bull. Chem. Soc. Japan, 1985, **58**, 2721.
151. A.N.Kasatkin and A.N.Kulak, Izv. Akad. Nauk SSSR, Ser. Khim., 1968, 2527.
152. G.Balme, G.Fournet, and J.Gore, Tetrahedron Lett., 1986, **27**, 3855.
153. A.Behr and U.Kanne, J. Organometal. Chem., 1986, **309**, 215.
154. A.Behr and W.Keim, Angew. Chem., 1985, **97**, 326.
155. J.Tsuj, T.Sugiura, M.Yuhara, and I.Minami, Chem. Communs., 1986, 922.
156. J.Tsuji, T.Sugiura, and I.Minami, Tetrahedron Lett., 1986, **27**, 731.
157. J.-C.Fiaud, B.Denner, and J.-L.Malleron, J. Organometal. Chem., 1985, **291**, 393.
158. Y.Inoue, S.Ajika, M.Toyofuka, et al., J. Mol. Catal., 1985, **32**, 91.
159. J.Tsuji, I.Minami, and I.Shimizu, Synthesis, 1986, 623.
160. P.M.Maitlis, "The Organic Chemistry of Palladium", Vol.2, Acad. Press, New York–London, 1971, 216 pp.
161. K.Itoh, "Fundamental Res. Organomet. Chem. Proc. China–Japan–US Trilaterial Semin.Peking, June, 1980", New York, Beijing, 1982, p.149.
162. V.A.Nikanorov, V.I.Rozenberg, A.I.Yanovsky, et al., J. Organometal. Chem., 1986, **307**, 363.

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