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CHEMISTRY OF PLATINUM AND PALLADIUM COMPOUNDS OF BULKY PHOSPHINES

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Despite much preparative work on transition metal compounds, two coordinate complexes still remained a rarity when we started to attempt their preparation. In order to achieve a low-coordination number, the strong propensity of transition metals to acquire the next higher inert gas configuration (18-electron rule) must be circumvented. An obvious strategy is to resort to steric bulk in the ligands. Wannagat et al. [1] some years ago prepared the remarkable compounds $Co[N(SiMe_3)_2]_2$, $Fe[N(SiMe_3)_2]_3$ etc.

The fact that some d^{10} transition metal ions such as Au^+ and Ag^+ form two coordinate compounds with such a sterically less demanding ligand as CN^- indicates the importance of the electronic structure of the metal center. Let us examine the theoretical basis of electronic factors.

The tendency of d^{10} Group IB metal ions to achieve low coordination numbers has been accounted for in terms of either the large energy separation between the $(n + 1)s$ and $(n + 1)p$ [2] or the small nd — $(n + 1)s$ separation [3]. It appears that the 18 electron rule has little quantum mechanical justification [4]. A recent theoretical analysis of the problem [5] indicates that the rule will be followed only when metal-to-ligand charge transfer supplements electron donation from the ligand. The phenomenological 16 or 18 electron rule proposed by Tolman [6] also lacks theoretical justification. On the other hand, Dewar-Chatt-Duncanson's bonding scheme and the underlying Pauling's electroneutrality principle have received support from recent quantum mechanical calculations [4,7].

We have been interested in preparation of two coordinate Pd^0 and Pt^0 compounds, a 14 electron system, which could be potential candidates for catalysts. Following Pauling's principle, for an electron rich metal center one must seek ligands of a biphilic nature, preferably with stronger electron donating properties. Hence we have chosen alkylphosphines rather than phosphites or isocyanides for the preparation of ML_2 (M = Pd, Pt), and this account briefly surveys the present status of our studies on the preparative and structural chemistry of such species. Also included is an account of the reactions of ML_2 with small molecules such as H_2, O_2, and olefins. A theoretical discussion of the extreme reactivity of bent ML_2 species is also presented. Some homogeneous catalytic reactions by ML_2 compounds have been described [8,9].

I. Existence of ML_2

The existence of ML_2 (M = Pt, Pd; L = PPh_3) has been postulated to account for the low molecular weight of $M(PPh_3)_4$ in solution [10]. Their existence as intermediates was also postulated in the substitution reactions of $Pt(PR_3)_2L$ (L = acetylene) [11]. A claim has been made for the existence of $Pt(PPh_3)_2$ [12], but this is doubtful in the light of the strong propensity to form polynuclear compounds such as $[Pt(PPh_3)_3]_2$ or $[Pt(PPh_3)_2]_3$ [13].

Table 1 lists the two coordinate phosphine complexes of the nickel triad metals so far isolated and well characterized. Obviously, steric bulk of the ligands plays a predominant role in stabilizing two coordination in a fourteen electron system. A measure of steric bulk proposed by Tolman [21] is the cone angle. Ligands with cone angles greater than 160° appear to favor two-coordination. Caution is necessary due to compressibility of the cone angle. In the bulky phosphines like $P(t\text{-}Bu)_3$ and $PPh(t\text{-}Bu)_2$, the size can be greatly squeezed (sometimes by more than 40%), as seen in Table 2.

II. Preparation and structure

In principle ML_2 (M = Pd, Pt) should be prepared by reduction of the corresponding MX_2L_2 with appropriate reducing agents such as sodium amalgam [18]. However, the reduction of $PdCl_2L_2$ (L = bulky tert-phosphines) with Na/Hg in THF is not successful, metallic palladium being formed. The reduction can be achieved with excess phosphine [17]. The sodium amalgam reduction is not applicable for the preparation of $Pt[P(t\text{-}Bu)_3]_2$, since $PtX_2[P(t\text{-}Bu)_3]_2$ is not accessible. Attempts to prepare $PtX_2[P(t\text{-}Bu)_3]_2$ from PtX_2 and $P(t\text{-}Bu)_3$ results in nearly complete reduction of Pt^{II} to platinum metal together with a small amount of $PtCl[P(t\text{-}Bu)_2C(CH_3)_2CH_2][P(t\text{-}Bu)_3]$.

TABLE 1

TWO COORDINATE COMPLEXES OF THE ZEROVALENT NICKEL TRIAD

Metal	Ligand	Ref.
Ni	$P(c\text{-}C_6H_{11})_3$ [a]	14
	$P(O\text{-}C_{10}H_{17})_3$ [b]	15
	$P(O\text{-}o\text{-}C_6H_4C_6H_5)_3$	16
Pd	$P(i\text{-}Pr)_3$	17
	$P(c\text{-}C_6H_{11})_3$	17
	$PPh(t\text{-}Bu)_2$	17, 18
	$P(t\text{-}Bu)_3$	18
Pt	$P(i\text{-}Pr)_3$	18
	$P(c\text{-}C_6H_{11})_3$	18, 19
	$PMe(t\text{-}Bu)_2$	20
	$PPh(t\text{-}Bu)_2$	18
	$P(t\text{-}Bu)_3$	18

[a] Not isolated. [b] $C_{10}H_{17}$ = bornan-2-yl.

TABLE 2

RELATION BETWEEN CONE ANGLE OF L AND COORDINATION NUMBER OF ML_n (M = Pd, Pt), AND COMPRESSIBILITY OF CONE ANGLE

Ligand	Cone angle (deg)	*n* found	Cone angle found
$P(t\text{-}Bu)_3$	182 ± 2	2	103 [a] in $RhH_2Cl[P(t\text{-}Bu)_3]_2$
$PPh(t\text{-}Bu)_2$	170 ± 2	2	100 [b] in *trans*-$MHCl[PPh(t\text{-}Bu)_2]_2$ (M = Pd, Pt)
$P(c\text{-}C_6H_{11})_3$	170 ± 10	2, 3	120 [c] in $Ni[P(c\text{-}C_6H_{11})_3]_3$
$P(O\text{-}o\text{-}C_6H_4CH_3)_3$	141, [d] 160 ± 10	3	109 [c] in $Ni[P(O\text{-}o\text{-}C_6H_4CH_3)_3]_4$
$P(i\text{-}Pr)_3$	160 ± 10	2, 3	120 [c] in $Pt[P(i\text{-}Pr)_3]_3$
PPh_3	145 ± 2	3, 4	109 [c] in $Pt(PPh_3)_4$
PEt_3	132 ± 4	3, 4	

[a] Evaluation based on the molecular parameters [42]. [b] Estimated assuming M—H and M—Cl bond lengths to be 1.65 and 2.3 Å respectively. [c] Formal valency angle; however, may be equivalent to cone angle. [d] In view of the nonexistence of tetracoordinate complex PtL_4 (L = $P(O\text{-}o\text{-}C_6H_4CH_3)_3$), the revised cone angle for $P(O\text{-}o\text{-}C_6H_4CH_3)_3$ seems too small since PtL_4 exists with PPh_3 whose cone angle was estimated to be 145 ± 2°.

An obvious alternative route is via substitution reactions. Thus, treating $Pd(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)$ [18] or $Pt(cod)_2$ (cod = 1,5-cyclooctadiene) [18,19,20] with phosphines gives the corresponding PdL_2 or PtL_2 in excellent yield.

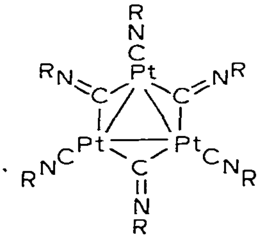
$$Pd(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5) + 2\,PR_3 \rightarrow Pd(PR_3)_2 + \text{hydrocarbons}$$

$$Pt(cod)_2 + PR_3 \rightarrow Pt(PR_3)_2 + 2\,cod$$

A phosphine ligand of medium steric bulk like $P(i\text{-}Pr)_3$ forms a tricoordinate compound PtL_3 which tends to dissociate one mole of L [17,18]. In such a case, it is possible to obtain PtL_2 from PtL_3 by thermal removal of L (see the following section).

It is noteworthy that the displacement reaction of $Pt(cod)_2$ with t-BuNC gives a trinuclear compound [19]. With alkyl isocyanides as ligands the tendency to assume a higher coordination is apparent. This result is not unexpected, as discussed in the preceding section.

$$Pt(cod)_2 + 2\,RNC = \frac{1}{3}$$



A few ML_2 compounds have been subjected to X-ray diffraction studies. Table 3 summarizes the most important structural parameters.

$Pd[P(c\text{-}C_6H_{11})_3]_2$ is noticeably bent but $M[PPh(t\text{-}Bu)_2]_2$ complexes are almost linear. There is no intrinsic reason to deviate from linearity in a ML_2 system having a metal of d^{10} non-bonding core. In view of the feeble $d\pi$ accepting character of tert-phosphines, especially trialkyl-phosphines, the bent structure may be taken to be an indication of the minor contribution of $d\pi$—$p\pi$ bonding relative to the σ-bonding in the M—P link. The bent structure in the solid state

TABLE 3

STRUCTURAL PARAMETERS OF ML_2

Compounds	av M—P distance (Å)	PMP angle (deg)	Ref.
$Pd[P(c\text{-}C_6H_{11})_3]_2$	2.26	158.4(3)	22
$Pd[PPh(t\text{-}Bu)_2]_2$	2.285(2)	176.6(1)	18, 22
$Pt[PPh(t\text{-}Bu)_2]_2$	2.252(1)	177.0(1)	18

may be a reflection of a shallow potential surface for bending. It should be added that $Pt[P(i\text{-}Pr)_3]_2$ assumes an essentially linear structure in solution as can be deduced from the virtual coupling of the methyl proton signal (^3J(H—P) + ^5J(H—P) = 14 Hz).

The M—P distances deserve comment. The most reasonable covalent radii of Pd^0 and Pt^0 we could estimate are 1.35 and 1.38 Å, respectively [18]. Taking the covalent radius of the P atom as 1.10 Å, we find that the sum of these covalent radii is much greater than the observed bond length in both PtL_2 and PdL_2. Also, the M—P bond length is shorter in PtL_2 than in the corresponding PdL_2 (Table 2). These features can be accounted for in terms of the $d\pi$—$d\pi$ back bonding. Pd^0 is a poorer $d\pi$ donor than Pt^0. The M—P bond length (2.252 Å) in $Pt[PPh(t\text{-}Bu)_2]_2$ is shorter than that (2.290 Å) in $PtO_2[PPh(t\text{-}Bu)_2]_2$ [23]. The opposite trend might have been expected in view of the increase in effective nuclear charge of the metal center upon conversion of PtL_2 to PtO_2L_2. The explanation may lie in the change of covalent radius of the metal which accompanies the change in hybridization.

III. Dissociative equilibria of PtL_n

It is pertinent to discuss here the dissociative behavior of PtL_n in solution as a function of ligand bulk.

The dissociation of $Pt(PEt_3)_4$ was studied in n-heptane and THF by electronic spectroscopy [9]. The K_1 value (eq. 1) at 20°C is 0.5 M in THF and 0.3 M in

$$Pt(PEt_3)_4 \overset{K_1}{\rightleftharpoons} Pt(PEt_3)_3 + PEt_3 \qquad (1)$$

n-heptane. Further dissociation to $Pt(PEt_3)_2$ is not detectable spectroscopically. By contrast, the dissociation of $Pt[P(i\text{-}Pr)_3]_3$ is extensive; K_2 (eq. 2) is

$$Pt[P(i\text{-}Pr)_3]_3 \overset{K_2}{\rightleftharpoons} Pt[P(i\text{-}Pr)_3]_2 + P(i\text{-}Pr)_3 \qquad (2)$$

1.4×10^{-1} M in THF and 4.0×10^{-2} M in n-heptane. About 94% of the complex ($Pt[P(i\text{-}Pr)_3]_3 = 9.8 \times 10^{-3}$ M) exists as $Pt[P(i\text{-}Pr)_3]_2$ in the absence of added phosphine in THF solution. In coordinating solvents such as pyridine the dissociation should be more extensive, but accurate measurement could not be made.

Steric effects appear to dominate the dissociation constant of ML_n. However, electronic effects of the ligands cannot be ignored. For example, the strong propensity of $Pt[P(i\text{-}Pr)_3]_3$ to dissociate one mole of $P(i\text{-}Pr)_3$ contrasts with the reluctance of $Pt[P(O\text{-}o\text{-}C_6H_4CH_3)_3]_3$ to undergo dissociation; both ligands have comparable cone angles, 160° vs. 165°(141°) [18].

The electronic properties of metal ions influence their preferred coordination number. For example, Ni^0 forms NiL_4 with $P(O\text{-}o\text{-}C_6H_4CH_3)_3$ [24] whereas Pt^0 with this phosphite forms PtL_3 only and shows no inclination to form PtL_4 in solution. This indicates that Ni^0 tends to assume a higher coordination number than Pd^0 or Pt^0. Such a trend has long been known for the triad, Cu^I, Ag^I, and Au^I.

The $d\pi$ donating property of nickel triad decreases in the order of Ni > Pt > Pd, as reflected in their promotional energy $d^{10} \rightarrow d^9p^1$; 1.72, 4.23 and 3.28 eV for Ni, Pd, and Pt, respectively [25]. Hence the above trend is also explainable on the basis of the powerful Pauling electroneutrality principle. Also the fact that the preferred two coordination of Pt^0 can be realized with the electron donating $P(i\text{-}Pr)_3$ rather than with a more electron accepting ligand can be under stood in terms of this principle. It is then evident that steric effects should be compared within a range of ligands having very similar electronic properties.

IV. Ligand exchange

The compressibility of steric bulk in tertiary phosphines is manifested in the formation of tetracoordinate compounds $PtHXL_2$ (X = monodentate ligands such as Cl or $OCOCF_3$) from PtL_2 where L is a very bulky phosphine such as $P(t\text{-}Bu)_3$ or $PPh(t\text{-}Bu)_2$ [26]. (Note that PtL_3 could not be prepared with such a bulky phosphine.) Ligand exchange, however, was observed between PtL_2 and L (L = $PPh(t\text{-}Bu)_2$, $P(c\text{-}C_6H_{11})_3$) [26]. A question then arises as to the mechanism of exchange.

A 1 : 3 mixture of $Pd[PPh(t\text{-}Bu)_2]_2$ and free $PPh(t\text{-}Bu)_2$ shows two tert-butyl proton signals at 35°C; one is a triplet (δ 1.45 ppm) assignable to the former and the other a doublet (δ 1.16 ppm) due to the latter. They begin to broaden at 60°C and coalesce around 120°C giving rise to an asymmetrical doublet, indicating intermolecular ligand exchange. The width of the lower field line of the triplet due to $Pd[PPh(t\text{-}Bu)_2]_2$ was found to be independent of the concentration of the complex and dependent on the free $PPh(t\text{-}Bu)_2$ concentration, whereas the width of the high-field line of the doublet due to free $PPh(t\text{-}Bu)_2$ is dependent on the concentration of the complex but independent of the free ligand concentration. Therefore, the exchange is first order with respect to the complex and free $PPh(t\text{-}Bu)_2$, implying an associative mechanism. This was rather surprising, however, since we found that the CPK molecular model for the three coordinate compound, $M[PPh(t\text{-}Bu)_2]_3$ (M = Pd, Pt) could not be made because the ligand bulk if an appropriate M—P distance (~2.3 Å) were retained.

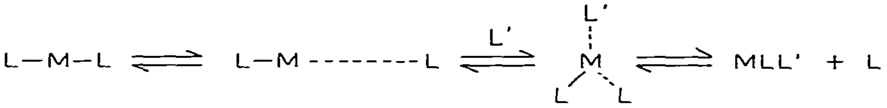
The temperature dependence of this intermolecular process was then compared for the Pd^0 and Pt^0 compounds. A higher temperature is required to observe the ligand exchange between $Pt[PPh(t\text{-}Bu)_2]_2$ and $PPh(t\text{-}Bu)_2$. The activation parameters are compared in Table 4. The large negative value of the activation entropy is consistent with the associative mechanism. A reasonable postulate then is that the exchange reaction occurs through a transition state involving loosening of a M—L bond with concomitant approach of the third L to M.

TABLE 4

ACTIVATION PARAMETERS FOR LIGAND EXCHANGE OF $M[PPh(t\text{-}Bu)_2]_2$

M	ΔH (kcal mol^{-1})	ΔS (eu)	ΔG (kcal mol^{-1})
Pd	7.8	−40.2	18.8
Pt	12.1	−29.3	20.1

This postulate seems compatible with the fact that the Pt—L bond is stronger than the Pd—L bond, as manifested in the bond distances 2.252(1) Å for $Pt[PPh(t\text{-}Bu)_2]_2$ vs. 2.285(2) Å for $Pd[PPh(t\text{-}Bu)_2]_2$.



It should be noted that the above experiment clearly excludes the possibility of the existence of a unicoordinate species M—L.

V. Bent ML_2

A qualitative Walsh diagram based on extended Hückel MO method is available (Figure 1) [27]. For simplicity, only σ-type orbitals (represented by *s* orbitals) are considered for the ligands. Two conspicuous features emerge as ML_2 becomes bent: (1) σ_g^*, comprized of an out-of-phase combination of mainly d_{z^2} and L_s, becomes stabilized and (2) one (b_1) of the non-bonding *d* orbitals (π_g) becomes sharply destabilized.

The character of the b_1 orbital merits comment. As ML_2 begins to bend (in the *xz* plane), the L_s orbitals start to mix with p_x and d_{xz}. As a result the two orthonormal p_x and d_{xz} hybridize. The mixing scheme is schematically illustrated below (note the in-phase combination of L_s and p_x and out-of-phase combination of L_s and d_{xz}). As the bending proceeds the p_x component in b_1 decreases while the d_{xz} character increases. Therefore, when the LML angle approaches 90° the metal orbital component in b_1 becomes almost entirely d_{xz}.

The diagram, albeit qualitative, indicates that d^{10} metal ions prefer a linear structure for ML_2 while d^8 ions prefer a bent structure. This prediction must be limited to ML_2 compounds where σ-bonding dominates the M—L bonds. No example is so far available for bent ML_2 of d^8 ions.

We attempted to prepare RhL_2^+ complexes with bulky phosphines such as $P(t\text{-}Bu)_3$, $PPh(t\text{-}Bu)_2$, and $P(c\text{-}C_6H_{11})_3$. The reduction with sodium amalgam of $RhCl_3 \cdot 3\ H_2O$ in the presence of an excess of phosphine in THF provides $RhHL_2$ ($L = P(t\text{-}Bu)_3$), $RhH(\eta^1\text{-}N_2)L_2$ ($L = P(t\text{-}Bu)_3$, $PPh(t\text{-}Bu)_2$) or $\{RhHL_2\}_2(\mu\text{-}N_2)$ ($L = P\text{-}(c\text{-}C_6H_{11})_3$, $P(i\text{-}Pr)_3$) [28—30]. The failure to obtain RhL_2^+ com-

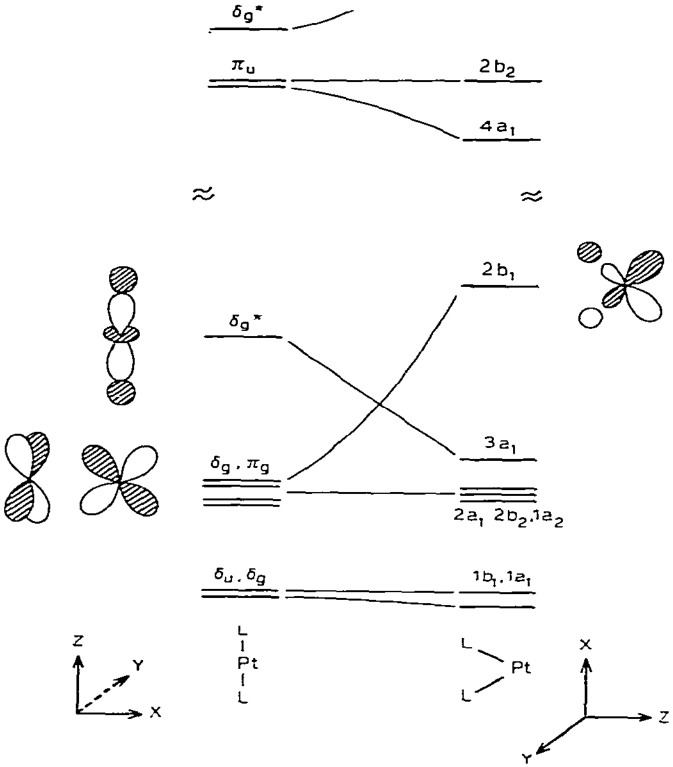


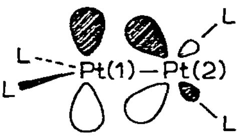
Fig. 1. Qualitative Walsh diagram of ML_2 with respect to its bending.

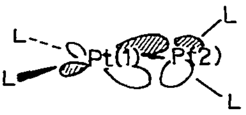
pounds reflects their extreme reactivity, which is presumably due to their bent structure exposing the valency orbitals.

It is then of interest to see if we could prepare bent ML_2 with d^{10} metals, which should behave as strong nucleophiles (Figure 1).

VI. Chelate diphosphine complexes

Reduction of $PtCl_2[(t\text{-}Bu)_2P(CH_2)_3P(t\text{-}Bu)_2]_2$ with sodium amalgam in THF at room temperature gives a deep red, binuclear compound $[Pt(t\text{-}Bu)_2P(CH_2)_3P(t\text{-}Bu)_2]_2$ [31]. The molecular structure, as revealed by an X-ray analysis, is shown in Figure 2. The coordination sphere of each Pt atom consists of a second Pt atom and two P atoms. The two coordination planes form a dihedral angle of 82°. The Pt—Pt distance 2.765(1) Å agrees with the value derived from the covalent radius, 1.38 Å, of Pt^0. Although a multiple metal—metal bonding scheme such as shown below is conceivable, the observed Pt—Pt distance indicates its minor contribution. The steric compression between the tert-butyl groups on the P atoms apparently forces the dihedral angles to be near 90°. However the two $5d\pi$—$6p\pi$ bonds, if they form, also favor the perpendicular configuration.





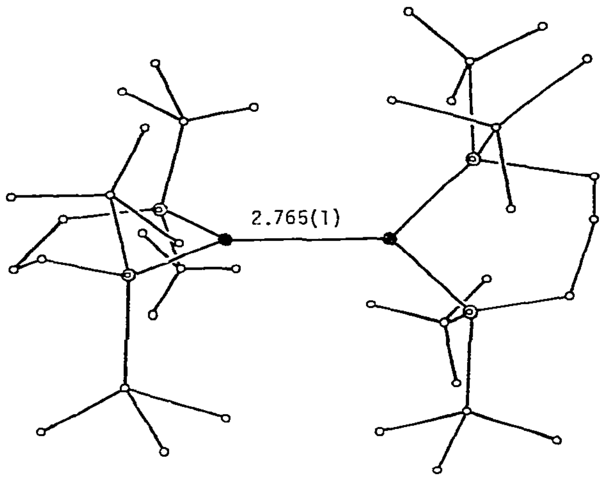
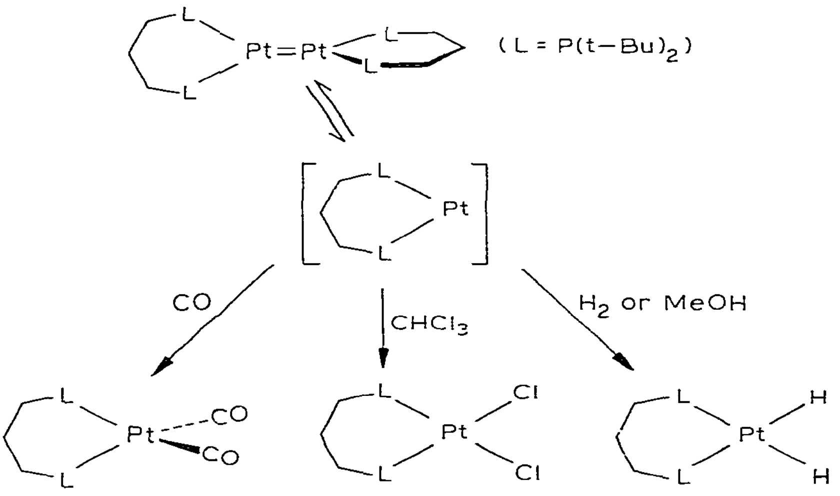


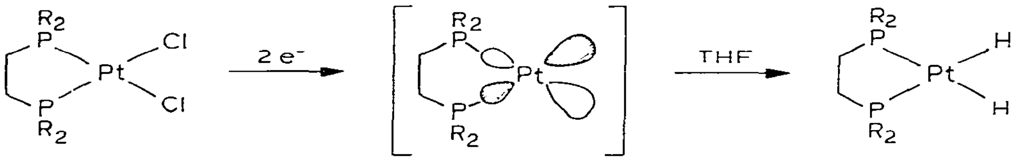
Fig. 2. Molecular structure of $[Pt(t\text{-}Bu)_2P(CH_2)_3P(t\text{-}Bu)_2]_2$; Pt—P distances, 2.272(1) and 2.268(2) Å, P—Pt—P angle, 102.6°(1).

The weakness of the Pt—Pt bond is manifested in the reactivity of the dimer [31]. Thus, Pt—Pt bond cleavage readily occurs with CO (1 atm), $CHCl_3$, H_2, etc. (Scheme 1). The reaction with MeOH also gives the *cis* dihydride. For example, addition of a few drops of methanol to the orange-red THF solution of the dimer causes slow discoloration at room temperature indicating oxidative addition. Inspection of a CPK molecular model of this Pt^0 dimer suggests that the bulk of the tert-butyl groups renders direct attack of a molecule such as methanol unlikely. Although no direct evidence for dissociation to a mononuclear species $Pt[(t\text{-}Bu)_2PCH_2CH_2CH_2P(t\text{-}Bu)_2]$ was obtained, the extreme instability in solution suggests the possibility of spontaneous Pt—Pt bond cleavage. Consistent with this, the mass spectrum shows a distinct peak for the mononuclear ion (*m/e* 527) along with the parent ion (*m/e* 1054).

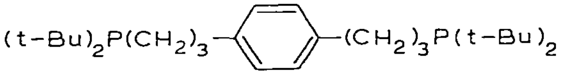
SCHEME 1



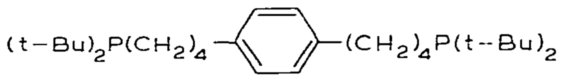
Attempts to prepare similar binuclear compounds with $R_2PCH_2CH_2PR_2$ (R = t-Bu, menthyl, etc.) were not successful. When a THF solution of $PtCl_2$-$[R_2PCH_2CH_2PR_2]$ was treated with Na/Hg, a dark red color developed. After filtration and concentration, the concentrate was still colored. However, the crystals precipitated upon cooling were colorless. In fact the crystalline product is the *cis* dihydride $PtH_2(R_2PCH_2CH_2PR_2)$ [31]. The source of the hydride ligands is doubtless THF. The result is understood in terms of the extremely strong nucleophilicity of the bent M(L—L) species. Note the sharp rise of filled $2b_1$ orbital as the PMP angle approaches 90° (Figure 1). The enhanced reactivity of the $Pt[R_2PCH_2CH_2PR_2]$ species precludes formation of the dinuclear compound observed for the $R_2PCH_2CH_2CH_2PR_2$ analog. These results demonstrate the dramatic effects of the inter-ligand-angle PMP on the reactivity of M(L—L) species.



Another attempt to obtain M(L—L) was made with diphosphines having a long chain between the phosphorus atoms. The diphosphines used were:



BPPB

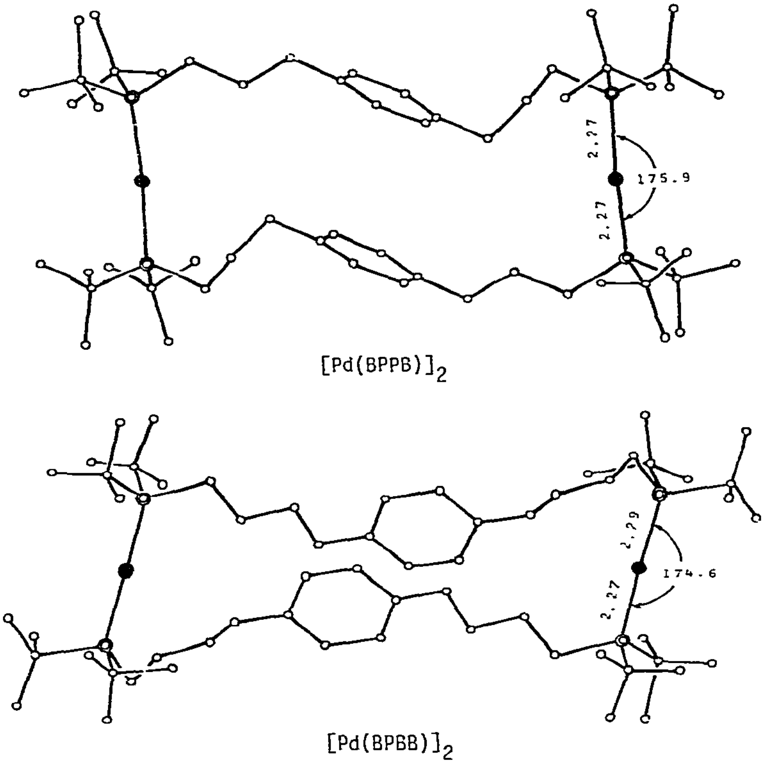


BPBB

Using the high dilution technique, the monomeric palladium(II) compounds, *trans*-$PdCl_2$(BPPB) and *trans*-$PdCl_2$(BPBB), were obtained by treating $PdCl_2$-$(PhCN)_2$ with these diphosphines in benzene. Their monomeric structure was confirmed by X-ray analysis, cryoscopic molecular weight measurements ($CHCl_3$), and vapor pressure osmometry [32].

Treating $Pd(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)$ similarly with these diphosphines in n-hexane gave palladium(0) compounds. Their elemental analyses corresponded to Pd-(L—L). They were not, however, the desired monomeric compounds, but were dimeric, as shown by cryoscopic molecular weight measurement in benzene and X-ray analysis [32]. $Pd_2(BPPB)_2$ and $Pd_2(BPBB)_2$ possess a nearly linear P—Pd—P structure (175 ~ 176°), as shown in Figure 3.

These dimeric palladium(0) compounds readily react with dioxygen in solution as well as in solid state (see paragraph VII), although they do not absorb dihydrogen. This is not unexpected since no palladium(0) compound has been reported to be capable of undergoing oxidative addition of dihydrogen. Therefore it was astonishing to find that a n-hexane solution containing a palladium(0) product formed in situ from $Pd(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)$ and BPPB did absorb dihydrogen. The reaction gave *trans*-PdH_2(BPPB) (ν(Pd—H) 1723 cm^{-1}; ^1H NMR δ 4.24 (t, Pd—H, J(HP) 6.6 Hz), 1.32 ppm (t, t-Bu, ^3J(P—H) + ^5J(P—H) 12.0 Hz)). The result strongly suggests initial formation of a reactive monomeric species Pd(BPPB) since the dimer does not react with dihydrogen. This monomeric



[Pd(BPPB)]$_2$

[Pd(BPBB)]$_2$

Fig. 3. Molecular structures of [Pd(t-Bu)$_2$P(CH$_2$)$_n$C$_6$H$_4$(CH$_2$)$_n$P(t-Bu)$_2$]$_2$ (n = 3, [Pd(BPPB)]$_2$; n = 4, [Pd(BPBB)]$_2$).

diphosphine palladium complex must have exhibited unprecedented reactivity toward dihydrogen.

VII. Reactions with dioxygen

The coordinatively unsaturated species ML_2 (M = Pt, Pd) are expected to undergo various addition reactions. However, with extremely bulky phosphines, addition to ML_2 is limited to small substrates, e.g. HX [26]. They do not accept two-center π-acids which require *cis*-alignment of the phosphine ligands. Thus oxidative addition of HX (X = H, Cl, OCOCF$_3$, etc.) readily occurs to give *trans*-MH(X)L$_2$ even with such a bulky phosphine such as P(t-Bu)$_3$.

M[P(t-Bu)$_3$]$_2$ (M = Pt, Pd) are quite inert to dioxygen. A slight reduction in bulk of phosphines raises the reactivity towards π-acids. Dioxygen complexation is observed for M[PPh(t-Bu)$_2$]$_2$ and M[P(c-C$_6$H$_{11}$)$_3$]$_2$ (cone angle, 179 ± 10° for both ligands). Unexpectedly the palladium complex readily loses dioxygen upon heating in vacuo to give back Pd[PPh(t-Bu)$_2$]$_2$ (60% isolated yield). The

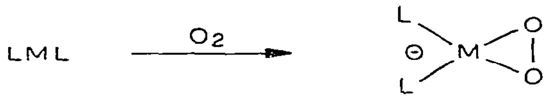


TABLE 5

IMPORTANT INTERATOMIC DISTANCES (Å) AND ANGLES (deg) in MO$_2$[PPh(t-Bu)$_2$]$_2$ (M = Pd, Pt)

Compound	M—O (Å)	O—O (Å)	M—P (Å)	P—M—P (deg)
PdO$_2$[PPh(t-Bu)$_2$]$_2$	2.05(2) 2.06(2)	1.37(2)	2.357(5) 2.360(5)	115.4
PtO$_2$[PPh(t-Bu)$_2$]$_2$	2.02(2) 2.02(2)	1.43(2)	2.290(4) 2.290(4)	113.1
PtO$_2$(PPh$_3$)$_2$ 1.5 C$_6$H$_6$	2.01(2) 2.01(3)	1.45(4)	2.282(11) 2.253(12)	101.2

platinum analog does not show such reversibility.

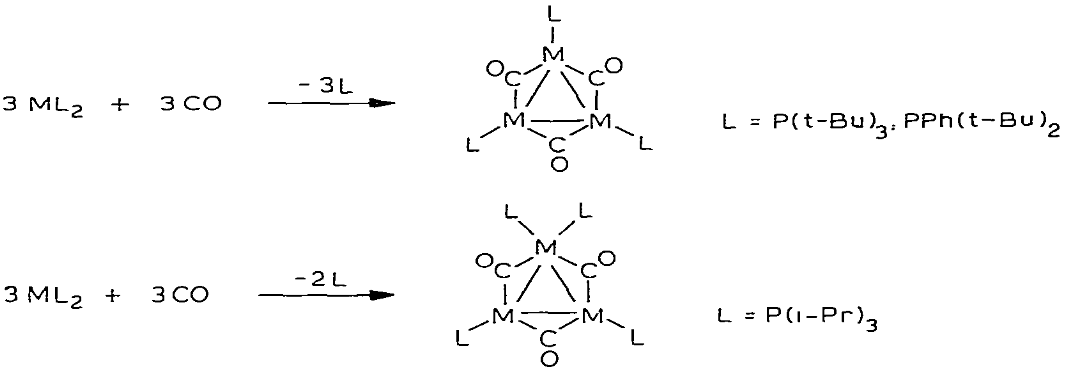
The two dioxygen compounds were then studied by X-ray analysis and MO calculations [23]. Their important structural parameters are compared with those of the known compound PtO$_2$(PPh$_3$)$_2$ [33] in Table 5. Salient features are: (1) the O—O and M—O distances are slightly longer for the reversible palladium compound than for the two irreversible platinum compounds, and (2) the P—M—P angle is slightly larger for the palladium compound than the platinum analog. Also the comparable O—O distances for the two platinum complexes are rather unexpected in view of the considerable difference in electronic properties of the two phosphines. In terms of the qualitative Dewar-Chatt-Duncanson π-back bonding scheme, the O—O bond length in PtO$_2$-[PPh(t-Bu)$_2$]$_2$ would be expected to be longer than that in PtO$_2$(PPh$_3$)$_2$ [33,34] because of the more enhanced back donation by PPh(t-Bu)$_2$ compared to that by PPh$_3$.

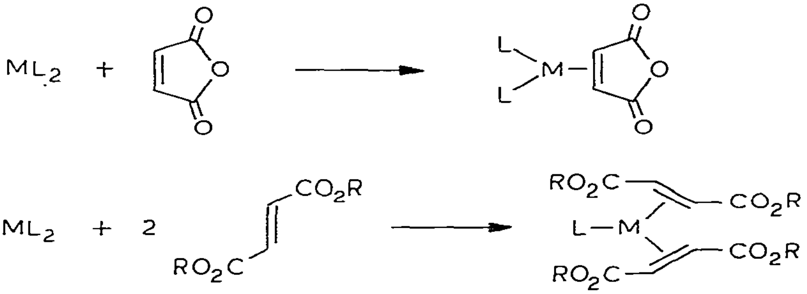
A rationalization was provided by the MO calculations of MO$_2$L$_2$ at the level of modified INDO approximation. The results may be briefly summarized as follows. (1) An enhanced electron donation of L causes weakening of the M—O covalent bonding in MO$_2$L$_2$. (2) The total energy shows a minimum at a certain PMP angle (107° in MO$_2$(PH$_3$)$_2$). Hence, a larger PMP angle destabilizes MO$_2$L$_2$. Note the larger P—M—P angle for PdO$_2$[PPh(t-Bu)$_2$]$_2$ compared to the platinum analog, albeit a small difference. A large L—M—L angle in PdO$_2$[PPh(t-Bu)$_2$]$_2$ causes ineffective charge transfer to O$_2$ resulting in an O—O distance comparable to that in PdO$_2$(PPh$_3$)$_3$. Thus, the inter-ligand angle θ of M(AA)L$_2$ (AA = two-center π-acid) exerts a stereoelectronic effect on the M—A and A—A bond strengths and hence their distances. This view receives support from the observed reversibility of [PdO$_2$(BPPB)]$_2$ and [PdO$_2$(BPBB)$_2$]$_2$.

VIII. Reactions with π-acids

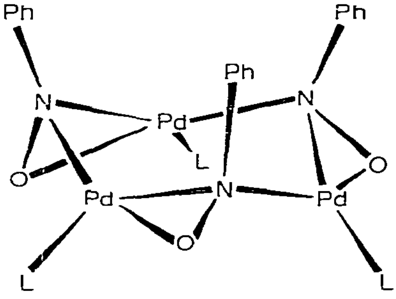
ML$_2$ readily reacts with various π-acids other than O$_2$ when L is not so extremely large as P(t-Bu)$_3$ [26]. Carbon monoxide, however, appears to be able to sneak into the coordination sphere of M[P(t-Bu)$_3$]$_2$ (M = Pd, Pt). Thus on bubbling CO into the n-hexane solution, trinuclear cluster compounds of formula M$_3$(CO)$_3$[P(t-Bu)$_3$]$_3$ are formed. Similar cluster compounds were obtained with M[PPh(t-Bu)$_2$]$_2$. In case of a less bulky P(i-Pr)$_3$ complex, PtL$_3$ reacts with CO giving Pt$_3$(CO)$_3$L$_4$.

Electrophilic olefins give two types of adducts. Sterically less demanding olefins, e.g. maleic anhydride, readily react with ML_2 ($L = PPh(t\text{-}Bu)_2$) to give $M(olefin)L_2$ quantitatively, while somewhat bulky olefins such as fumarate react more slowly with PtL_2 to give $M(olefin)_2L$ ($M = Pd, Pt$; $L = PPh(t\text{-}Bu)_2$). Both types of olefin complexes are already known. In these compounds, coplanar coordination of the double bond(s) in the coordination plane is probable. The coplanar coordination of three olefinic ligands has been established by X-ray analysis for Ni(bicyclo[2,2,1]heptene)$_3$ [35]. The in-plane alignment in $Ni(CH_2{=}CH_2)_3$ was found by extended Hückel MO calculation to be a preferred coordination configuration [36]. This was confirmed by X-ray analysis of $Pt(CH_2{=}CH_2)_2(CF_2{=}CF_2)$ [37].





Nitrosobenzene can act as a two-center π-acid. Thus mononuclear compounds, $M(\eta^2\text{-}ONC_6H_5)(PPh_3)_2$ ($M = Ni, Pd, Pt$) were obtained from $M(CH_2{=}CH_2)(PPh_3)_2$ [38]. Interestingly, the reaction of PhNO with two-coordinate compounds PdL_2 ($L = P(t\text{-}Bu)_3$, $PPh(t\text{-}Bu)_2$) gave a trinuclear compound of formula $Pd_3L_3(PhNO)_3$. The structure shown below was determined by X-ray analysis [39].



IX. Oxidative addition of water

Studies on the reaction of water with zerovalent platinum complexes PtL_n ($n = 2,3$) have led to the evolution of a fascinating chemistry of strong hydroxo basis [9].

Oxidative addition of H_2O to low-valent transition metal compounds was expected to occur since H_2O is a stronger acid ($pK_a = 15.7$) than MeOH ($pK_a = 17.7$) which undergoes a facile oxidative addition to PtL_n ($n = 2,3$; L = tert-phosphines). The addition, however, has been reported for only a very few cases, e.g. formation of $Os_3H(OH)(CO)_{10}$ from $Os_3(CO)_{12}$ [40] and $[RhH(OH)en]^+$ from $[Rh(en)_2]^+$ [41]. The chemistry of the hydridohydroxo metal compound remained virtually unexplored prior to our studies.

Successful isolation of the adduct, *trans*-$PtH(OH)L_2$ is possible only by treating bis-phosphine complexes PtL_2 ($L = P(i\text{-}Pr)_3$) with a large excess of water in an organic solvent like THF. The colorless adduct $PtH(OH)[P(i\text{-}Pr)_3]_2$ (Pt—H, δ —20.0 ppm, t, J(H—P) 14.4 Hz, J(H—Pt) = 944 Hz) is extremely air sensitive and thermally unstable, decomposing slowly in dry saturated hydrocarbons or even in the solid state at room temperature.

The reaction with trisphosphine compounds PtL_3 ($L = PEt_3$, $P(i\text{-}Pr)_3$) occurs only in a coordinating solvent such as pyridine, affording ionic compounds $[PtH(S)L_2]OH$ (S = solvent) which can be isolated as $[PtH(S)L_2]BF_4$.

Apparent pH values of system PtL_3/H_2O measured in THF and pyridine are compared with those of NaOH in Table 6. It is noteworthy that PtL_3 behaves as a stronger base than NaOH in aqueous organic media. *trans*-$Pt(OH)(Ph)(PPh_3)_2$ also acts as a comparable base (pH = 14.1) in aqueous pyridine but the pH value is lower (8.2) in aqueous THF. These results clearly imply weak bonding between the hard OH^- and soft Pt^{II} ions.

The solution behavior of the $Pt(PEt_3)_3$ system in aqueous THF or pyridine can be described in terms of equilibria 3 and 4. The equilibrium

$$Pt(PEt_3)_3 + H_2O \overset{K_0}{\rightleftharpoons} PtH(PEt_3)_3^+OH^- \qquad (3)$$

$$PtH(PEt_3)_3^+OH^- \overset{K_d}{\rightleftharpoons} PtH(PEt_3)_3^+ + OH^- \qquad (4)$$

constants in pyridine at 0.5°C were assessed from Fuoss treatments of the conductivity data; $K_0 = 0.6(\pm 0.3)\ \text{mol}^{-1}\ \text{l}$, $K_d = 4.2(\pm 0.2) \times 10^{-2}\ \text{mol l}^{-1}$. The equili-

TABLE 6

APPARENT pH OF SYSTEM PtL_3/H_2O IN THF AND PYRIDINE

Compounds	pH_{app} [a]	
	in THF [b]	in Pyridine
$Pt(PEt_3)_3$	14.0	14.3
$Pt[P(i\text{-}Pr)_3]_3$	12.9	14.1
NaOH	13.5	13.5

[a] [Complex] = [NaOH] = 9.8×10^{-3} *M*. Volume ratio of H_2O vs. THF or pyridine was 2 : 3. Measured at 20°C. [b] Apparent pH's of PEt_3 and $P(i\text{-}Pr)_3$ (9.8×10^{-3} *M*) were 9.9 and 8.6, respectively.

bria involved in the $Pt[P(i\text{-}Pr)_3]_3/H_2O$ system are more complex. The solution behavior is satisfactorily described in terms of four equilibria 5—8.

$$PtL_3 \overset{K_L}{\rightleftharpoons} PtL_2 + L \tag{5}$$

$$PtL_2 + H_2O \overset{K_0}{\rightleftharpoons} PtH(OH)L_2 \tag{6}$$

$$PtH(OH)L_2 + S \overset{K_s}{\rightleftharpoons} PtH(S)L_2^+OH^- \tag{7}$$

$$PtH(S)L_2^+OH^- \overset{K_d}{\rightleftharpoons} PtH(S)L_2^+ + OH^- \tag{8}$$

Assuming complete dissociation of $Pt[P(i\text{-}Pr)_3]_3$ into $Pt[P(i\text{-}Pr)_3]_2$ and $P(i\text{-}Pr)_3$ in the coordinating solvent (pyridine), a similar treatment has led to a satisfactory analysis of the conductivity data. In this case the individual constants cannot be determined. Instead the values of composite constants were obtained; $(1 + K_s) K_0 = 0.1(0.06)$ mol^{-1} l, $K_sK_d/(1 + K_s) = 1.2(0.1) \times 10^{-1}$ mol l^{-1}.

Since $(1 + K_s)$ is greater than 1, the value of K_0 for the $Pt[P(i\text{-}Pr)_3]_3$ must be considerably smaller than for $Pt(PEt_3)_3$. This suggests that oxidative addition of H_2O to the tris-phosphine compound $Pt(PEt_3)_3$ to be more favorable than that to the bis-phosphine compound $Pt[P(i\text{-}Pr)_3]_2$. This seems reasonable, since the metal basicity should be greater with three than with two phosphine ligands of comparable electronic properties.

The strong basicity of systems PtL_n/H_2O in organic media suggests various applications. It has already been found that the systems can serve as catalysis for the water-gas shift reaction [8], hydration of electrophilic unsaturated bonds [9], and H—D exchange reactions of activated C—H groups with D_2O [9]. Various other uses in the field of organic syntheses should be possible.

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