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(54) $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = [\Sigma w_i||F_o| - |F_c||^2/\Sigma w_i|F_o|^2]^{1/2}$.

(55) Reference 52, Vol. III, 1962, p 215.

Reactions of Two-Coordinate Phosphine Platinum(0) and Palladium(0) Compounds. Ligand Exchange and Reactivities toward Small Molecules

T. Yoshida and Sei Otsuka*

Contribution from the Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka, Japan 560. *Received August 13, 1976*

Abstract: Reactions of two-coordinate complexes PdL_2 (**1**, L = $P(t\text{-Bu})_3$; **2**, L = $PPh(t\text{-Bu})_2$; **3**, L = $P(c\text{-}C_6H_{11})_3$) and PtL_2 (**4**, L = $P(t\text{-Bu})_3$; **5**, L = $PPh(t\text{-Bu})_2$; **6**, L = $P(c\text{-}C_6H_{11})_3$; **7**, L = $P(i\text{-Pr})_3$) were studied. The thermal reaction of **2** and **5** gives no evidence for ortho C metalation. Ligand exchange of **2** and **5** with $PPh(t\text{-Bu})_2$ takes place through an associative mechanism at high temperature with activation energies of 7.8 and 12.1 kcal mol^{-1}, respectively. These complexes, except **1** and **4**, are sensitive to dioxygen and react even in the solid state to produce MO_2L_2. Dioxygen coordination in $PdO_2[PPh(t\text{-Bu})_2]_2$ is reversible, while that in the corresponding Pt complex is irreversible. **1** reacts very slowly with dioxygen to give a red polynuclear oxygen-containing compound of formula $[PdOP(t\text{-Bu})_3]_n$. The reaction of **1**, **2**, and **5** with CO gives $M_3(CO)_3L_3$ (M = Pd, L = $P(t\text{-Bu})_3$, $PPh(t\text{-Bu})_2$; M = Pt, L = $PPh(t\text{-Bu})_2$). Dimethyl fumarate (DF) with **2** or **5** gives $M(DF)_2PPh(t\text{-Bu})_2$ (M = Pd, Pt), while maleic anhydride (MA) affords $M(MA)[PPh(t\text{-Bu})_2]_2$. Oxidative addition of HX (X = Cl, $OCOCF_3$) to **1**, **2**, and **5** produces *trans*-$MH(X)L_2$ (M = Pd, L = $P(t\text{-Bu})_3$, $PPh(t\text{-Bu})_2$; M = Pt, L = $PPh(t\text{-Bu})_2$). MeOH reacts with PtL_2 to give stable dihydride complexes *trans*-PtH_2L_2 (L = $PPh(t\text{-Bu})_2$, $P(c\text{-}C_6H_{11})_3$, $P(i\text{-Pr})_3$), which can be obtained also by molecular hydrogen addition to the appropriate PtL_2 at room temperature under normal pressure. **4** and **5** do not add H_2. All the PdL_2 complexes are inert toward MeOH and H_2. Factors determining the observed reactivities of these ML_2 complexes are discussed in terms of steric and electronic effects.

In previous papers[1,2] we reported syntheses of two-coordinate complexes ML_2 (Table I) and the molecular structures of **2** and **5**. The successful isolation is possible because of the stability of these complexes in solution. The x-ray analysis of $PPh(t\text{-Bu})_2$ complexes **2** and **5** revealed nonbonding contacts (2.7 ~ 2.8 Å) of ligand hydrogen atoms to the metals, which apparently prevent approach of solvent molecules.[2] The extent of kinetic stabilization in this series depends critically upon the ligand bulk. For example, complexes of exceedingly bulky $P(t\text{-Bu})_3$ (cone angle[3] 182°), **1** and **4**, are fairly air stable in the solid state, while all the other ML_2 compounds are readily dioxygenated. The two-coordinate complexes of moderately bulky phosphines (cone angle <170°) exhibit high reactivity toward small molecules such as H_2, CO, HX (X = halogen, RCO_2, RO), olefins, etc. Even when the cone angle of phosphines in ML_2 exceeds 170°, four-coordinate complexes $MH(X)L_2$ are formed, suggesting considerable ligand compressibility.[2] Enhanced reactivity can thus be expected for most of the ML_2 complexes. The electronic properties of both the ligand and the metal also influence the reactivity. With strongly electron-donating phosphines it is possible to prepare ML_2 capable of absorbing a hydrogen molecule under normal pressure, a phenomenon unusual for Pd(0) or Pt(0) compounds.[4] In this paper the reactivity of ML_2 species toward a wide range of compounds will be described and discussed in terms of steric and electronic factors.

It has been recognized that the reactivity, particularly substitution, of coordinatively saturated complexes ML_4 is governed by the propensity for dissociation to form ML_3 and ML_2 species.[4-7] Tolman[8] has stressed the importance of the 16- and 18-electron rule and argued against dissociation of NiL_3. It is then of interest to examine mechanisms of ligand exchange reactions in the present ML_2 system.

Results and Discussion

Innate Reactivity and Ligand Exchange. The short nonbonded contacts (2.83 Å)[1,2] between the metal and two hydrogen atoms of the phenyl groups in the solid and solution state (at low temperature) prompted us to examine if the thermal reaction of **2** and **5** leads to the aromatic substitution.[9,10] Prolonged heating of **2** and **5** in xylene under gentle reflux results in the decomposition of **2** or the complete recovery of **5** and no evidence for ortho C metalation is obtained. This contrasts to a facile metalation of the corresponding divalent complex $PtCl_2[PPh(t\text{-Bu})_2]_2$[11] and suggests that the facile intramolecular aromatic substitution occurs through a mechanism involving electrophilic substitution by metal[9,10,12] rather than an electrophilic, oxidative addition of the C–H to metal.[9,10,13] In support of this view, facile ortho C metalation of azobenzene occurs upon complexation with divalent nickel triad metal, e.g., $Ni(\eta^5\text{-}C_5H_5)_2$[14] and $PdCl_2$,[12] whereas the zerovalent complexes, $Ni(t\text{-BuNC})_2$[15] and $Ni(PPh_3)_4$[16] give side-on coordination $Ni(\eta^2\text{-PhN=NPh})L_2$ (L = t-BuNC, PPh_3).

In view of the compressibility of these tertiary phosphine ligands, we were initially interested in the maximum or minimum coordination number that can be seen in isolable species. With $P(i\text{-Pr})_3$ (cone angle, 160 ± 10°[3]) both PtL_2 (**7**) and PtL_3 (**8**) complexes could be obtained, but not the PtL_4.[2] With $PPh(t\text{-Bu})_2$ (cone angle, 170 ± 2°[2]) only ML_2 (**2**, M = Pd; **5**, M = Pt) was isolated, but not ML_3. Their absence was confirmed by ^1H NMR of a mixture of free $PPh(t\text{-Bu})_2$ and **2** or **5** recorded as low as −80 °C.[2,17] Interestingly, however, slow ligand exchange was observed in benzene or anisole at high temperature. A 1:3 mixture of **2** and $PPh(t\text{-Bu})_2$ shows the *tert*-butyl proton signals of **2** as a sharp triplet (δ 1.45) and

Table I. Designation of ML_2

Formula no.	1	2	3	4	5	6	7
M	Pd	Pd	Pd	Pt	Pt	Pt	Pt
L	$P(t\text{-}Bu)_3$	$PPh(t\text{-}Bu)_2$	$P(c\text{-}C_6H_{11})_3$	$P(t\text{-}Bu)_3$	$PPh(t\text{-}Bu)_2$	$P(c\text{-}C_6H_{11})_3$	$P(i\text{-}Pr)_3$

Table II. Activation Parameters for Ligand Exchange of $M[PPh(t\text{-}Bu)_2]_2$

	$\Delta H^{\ddagger}$, kcal mol^{-1}	log A, mol^{-1} s^{-1}	$\Delta S_0^{\ddagger}$, eu	$\Delta G_0^{\ddagger}$, kcal mol^{-1}
Pd	7.8	4.0	−40.2	18.8
Pt	12.1	6.3	−29.3	20.1

those of free $PPh(t\text{-}Bu)_2$ as a doublet (δ 1.16) at 35 °C (Figure 1). They begin to broaden at 60 °C, and at 110 °C the triplet completely collapses to a very broad signal with further broadening of the doublet. At 120 °C the two signals nearly coalesce, giving rise to a broad doublet. Further temperature increase was impossible due to the partial decomposition of **2**.

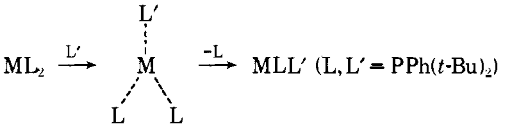
The exchange mechanism was studied by the temperature-dependent ^{1}H NMR. The width of the lowest field line of the triplet due to **2** was found to be independent on the complex concentration and dependent on the free ligand concentration, while the width of the high-field line of the doublet due to free $PPh(t\text{-}Bu)_2$ is dependent on the complex concentration and independent on the free ligand concentration. Thus the rates of exchange, $1/\tau_c$ and $1/\tau_f$, can be expressed by

$$1/\tau_c = k[PPh(t\text{-}Bu)_2]$$

$$1/\tau_f = k[Pd[PPh(t\text{-}Bu)_2]_2]$$

where τ_c and τ_f are the average lifetime of the coordinated and free $PPh(t\text{-}Bu)_2$, respectively. Therefore the reaction is first order with respect to **2** and free $PPh(t\text{-}Bu)_2$, suggesting an associative mechanism.

The ligand exchange reaction of Pt analogue **5** takes place at a higher temperature. Thus, the *tert*-butyl proton signals of a mixture of **5** (8.6×10^{-2} M) and $PPh(t\text{-}Bu)_2$ (5.7×10^{-1} M) in anisole begin to broaden above 80 °C, but they do not coalesce even at 150 °C. Activation parameters are compared in Table II. The negative activation entropies, $\Delta S_0^{\ddagger}$, are consistent with an associative process. A molecular model, however, reveals that three coordination is impossible for the bulky phosphine $PPh(t\text{-}Bu)_2$ when a reasonable metal-phosphorus distance (~2.3 Å) is retained. Since the covalent radius of Pd(0) is comparable to that of Pt(0),[2] the low activation energy for **2** (7.8 kcal mol^{-1}) compared with **5** (12.1 kcal mol^{-1}) cannot be explained purely by steric effect. A rationale may be found in the difference in M-P bond strength. The Pt-P bond distance in **5** of 2.252 (1) Å is shorter than the Pd-P distance (2.285 (2) Å) in the palladium analogue **2**, suggesting a more tenacious Pt-P bond.[2] A reasonable postulate then is that the Pd-P bond in **2** would become loose at high temperature so as to relax the steric crowding around the metal, while the tenacity of the Pt-P bond in **5** would require a higher activation energy than **2** to allow approach of the third ligand. Accepting this postulate, the slow exchange of $PPh(t\text{-}Bu)_2$ in **2** and **5** is accounted for with a transition state involving a loose association of $PPh(t\text{-}Bu)_2$.



$$ML_2 \xrightarrow{L'} \overset{L'}{\underset{L\quad L}{M}} \xrightarrow{-L} MLL' \quad (L, L' = PPh(t\text{-}Bu)_2)$$

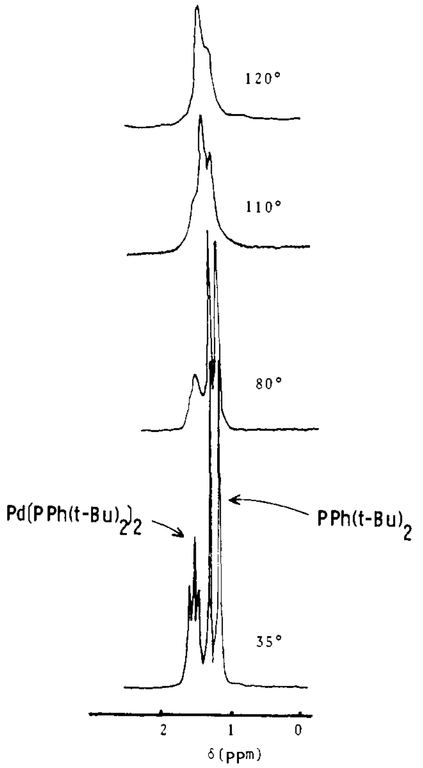


Figure 1. Temperature-variant ^{1}H NMR of $Pd[PPh(t\text{-}Bu)_2]_2$–$3PPh(t\text{-}Bu)_2$ in anisole.

Addition and Substitution. Surprisingly **1** and **4** are stable toward dioxygen in the solid state. Although molecular models reveal almost complete coverage of the metal atom with the *tert*-butyl hydrogen atoms, it does not seem impossible to accommodate the small dioxygen molecule as a monodentate ligand. However, the low temperature ^{1}H NMR of a toluene-d_8 solution of **1** or **4** under dioxygen shows no indication for existence of a paramagnetic species. At high temperature (>20 °C) **1** in n-hexane reacts slowly with dioxygen affording a reddish solution, from which brick red crystals of composition of $[PdOP(t\text{-}Bu)_3]_n$ can be isolated in extremely low yield. The IR spectrum shows no ν(O-O) expected for side-on coordination of dioxygen and the ^{1}H NMR is too complex to assign a reasonable structure to the polynuclear compound. An x-ray analysis will be required to elucidate the structure.

The two-coordinate complexes with less bulky phosphines, $PPh(t\text{-}Bu)_2$ and $P(c\text{-}C_6H_{11})_3$ (cone angle,[3] 179 ± 10°), readily absorb dioxygen. Thus **2** and **3** react with dioxygen even in the solid state as well as in n-hexane to afford PdO_2L_2 (**9**, L = $PPh(t\text{-}Bu)_2$; **10**, L = $P(c\text{-}C_6H_{11})_3$) quantitatively as diamagnetic green crystals. Similarly, **5** and **6** give the corresponding dioxygen complexes PtO_2L_2 (**11**, L = $PPh(t\text{-}Bu)_2$; **12**, L = $P(c\text{-}C_6H_{11})_3$) as pale brown crystals. They are soluble in methanol and benzene, but insoluble in the saturated hydrocarbons. The dioxygen complexes show the characteristic ν(O-O) in the region (Table III) observed for the triphenyl-

$$ML_2 \xrightarrow{O_2} MO_2L_2$$

$$M = Pd;\ L = PPh(t\text{-}Bu)_2,\ P(c\text{-}C_6H_{11})_3$$

$$M = Pt;\ L = PPh(t\text{-}Bu)_2,\ P(c\text{-}C_6H_{11})_3$$

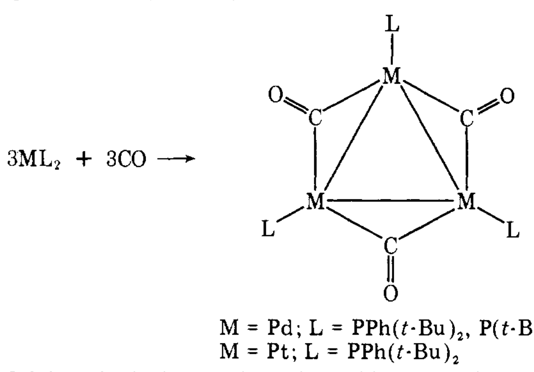
Table III. Spectral Data of Dioxygen Complexes

	^{1}H NMR[a,b] δ, ppm (Me_4Si)	Intensity	Assignment	IR, cm^{-1} [c] ν(O–O)
$PdO_2[PPh(t\text{-}Bu)_2]_2$ (**9**)	1.47 (d, $J_{H\text{-}P}$ = 13.2 Hz)	18	*t*-Bu	915
	7.55 (br t)	2	*o*-H	
	6.8 (m)	3	*m*- and *p*-H	
$PdO_2[P(c\text{-}C_6H_{11})_3]_2$ (**10**)	0.64 ~ 2.80 (m)		c-C_6H_{11}	900
$PtO_2[PPh(t\text{-}Bu)_2]_2$ (**11**)	1.41 (d, $J_{H\text{-}P}$ = 13.7 Hz)	18	*t*-Bu	835
	7.52 (br t)	2	*o*-H	
	6.92 (m)	3	*m*- and *p*-H	
$PtO_2[P(c\text{-}C_6H_{11})_3]_2$ (**12**)	0.60 ~ 2.80 (m)		c-C_6H_{11}	820

[a] Measured in benzene-d_6 at 22.5 °C. [b] Key: d, doublet; br t, broad triplet; m, multiplet. [c] Measured in Nujol mull.

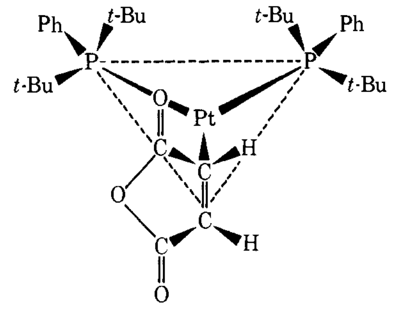
phosphine analogues[18] (880 cm^{-1} for $PdO_2(PPh_3)_2$, 830 cm^{-1} for $PtO_2(PPh_3)_2$). A bent P–M–P bond is deduced from a doublet pattern of *tert*-butyl proton signals for **9** and **11**. *trans*-$MHX[PPh(t\text{-}Bu)_2]_2$ complexes show this resonance as a triplet due to virtual coupling (vide infra). Side-on coordination of dioxygen is evident and confirmed by single-crystal x-ray analysis for **9** and **11**.[19] The cis alignment of these phosphine ligands in essentially square-planar compounds is rather surprising in view of their steric bulk (cone angle 170°). The green palladium complexes **9** and **10** are stable for several months below −10 °C, but decompose at room temperature in the solid state after standing for few days. **9** liberates dioxygen on heating under reflux in methanol or in vacuo at 60–70 °C to give the two-coordinate zerovalent complex **2**. This is rather remarkable since $PdO_2(PPh_3)_2$ decomposes to the free metal and Ph_3PO.[20] In sharp contrast to the palladium complex, the corresponding platinum complex **11** is stable under the same conditions.

On bubbling CO through a *n*-hexane solution of **1** and **2** at room temperature, $Pd_3(CO)_3L_3$ (**13**, L = $P(t\text{-}Bu)_3$; **14**, L = $PPh(t\text{-}Bu)_2$) precipitates immediately as yellow crystals. Similarly **5** gives $Pt_3(CO)_3[PPh(t\text{-}Bu)_2]_3$ (**15**) as orange crystals. The ^{1}H NMR spectra of these cluster compounds show a single *tert*-butyl proton signal as a doublet, implying equivalence of the three phosphines. The IR spectra indicate the presence of only bridging CO groups. The observation of two ν(CO) bands (Table IV) is consistent with D_{3h} symmetry. Similar complexes of Pd and Pt are known for the less bulky phosphines $PPh_2(CH_2Ph)$ and PPh_3.[21,22]

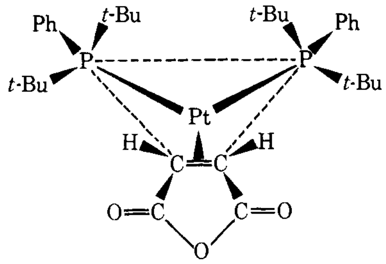


M = Pd; L = $PPh(t\text{-}Bu)_2$, $P(t\text{-}Bu)_3$
M = Pt; L = $PPh(t\text{-}Bu)_2$

Maleic anhydride (MA) readily adds to **2** and **5** at 30–40 °C in *n*-hexane to give quantitatively the corresponding olefin complexes $M(MA)[PPh(t\text{-}Bu)_2]_2$ (**16**, M = Pd; **17**, M = Pt). Their IR spectra (Table IV) show CO stretching frequencies in a region (1725–1795 cm^{-1}) comparable to those found in $M(MA)(t\text{-}BuNC)_2$ (M = Ni, Pd).[23] The *tert*-butyl and olefinic proton signals of **16** are a doublet and singlet, respectively. In contrast, platinum complex **17** gives rise to two doublets of equal intensity for the *tert*-butyl protons and one doublet for the olefinic protons due to a strong coupling with one phosphorus atom (Table IV), suggesting nonequivalence of the two *tert*-butyl groups and equivalence of the two olefinic protons. These spectral data are consistent with a perpendicular coordination of MA with respect to the molecular plane (**17a**). Alternatively, a planar coordination of MA as in **17b** is also possible if rotation of the phosphorus substituents is restricted. The conclusion is deferred in the absence of an x-ray structure analysis.



17a



17b

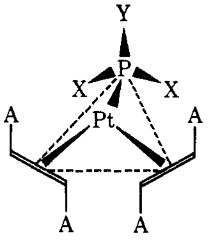
A reaction of dimethyl fumarate (DF) with **2** under similar conditions (30–40 °C) employed for MA gives a mixture of complexes including the starting materials. On prolonged heating (17 h) in toluene at 70–80 °C the above mixture gives the bis(olefin)monophosphine complex $Pd(DF)_2PPh(t\text{-}Bu)_2$ (**18**) as colorless crystals. A similar reaction of **5** with DF gives the corresponding Pt(0) complex $Pt(DF)_2PPh(t\text{-}Bu)_2$ (**19**). This type of olefin complex is known for Ni(0), Pd(0), and Pt(0), e.g., $M(CH_2{=}CH_2)_2P(c\text{-}C_6H_{11})_3$ (M = Ni,[24] Pd,[25] Pt[25]).

The observation of two types of olefinic and methyl proton resonances for **19** (Table IV) implies a rigid structure for which four isomers **19a–d** are possible. Structures **19a** and **19b** have C_s symmetry and **19c** and **19d** C_1 symmetry. For the structures of C_1 the two *tert*-butyl groups should be magnetically inequivalent (diastereotopic). The *tert*-butyl protons give rise to only one doublet resonance. The ^{13}C NMR (see Experimental Section) revealed two resonances each with identical coupling constant ($J_{C\text{-}P}$); viz. 36.8 and 36.9 ppm ($J_{C\text{-}P}$ = 19.3 Hz) for tertiary carbons and 29.8 and 30.2 ppm ($J_{C\text{-}P}$ = 15.6 Hz) for the *C*-methyl carbons. This points to structure **19c** or **19d**. Apparently the single *tert*-butyl proton resonance is due to fortuitous coincidence of the two resonances. Consistently the ^{13}C NMR also shows two different olefinic, carboxyl, and ester methyl carbon resonances. Dichotomy between **19c** and **19d** cannot be achieved by the ^{1}H and ^{13}C NMR results. According to a noniterative extended Hückel MO calculation on total energies of $Ni(CH_2{=}CH_2)_3$[26] and $Pt(CH_2{=}CH_2)(PH_3)_2$,[27] the *in-plane* coordination of olefins is more stable than the *perpendicular* coordination. A coplanar coordination of two

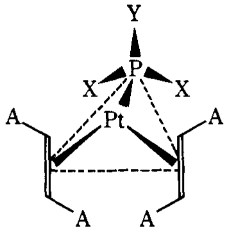
Table IV. Spectral Data of π-Acid Complexes

	^{1}H NMR, δ (ppm, Me_4Si)[a]			IR, cm^{-1} [b]
	t-Bu	J_{H-P}, Hz	Other	ν(CO)
$Pd_3(CO)_3[(t\text{-}Bu)_3]_3$ (**13**)	1.52 (d)	10.0		1843, s, 1802 s, 1795 s
$Pd_2(CO)_3[PPh(t\text{-}Bu)_2]_3$ (**14**)	1.42 (d, 18)	11.2	*o*-H, 7.90 (br, 2); *m*- and *p*-H, 7.23 (m, 3)	1870 s, 1832 vs, 1820 vs (1872 w, 1823 s)[c]
$Pt_3(CO)_3[PPh(t\text{-}Bu)_2]_3$ (**15**)	1.42 (d, 18)	13.2	*o*-H, 7.98 (br, s); *m*- and *p*-H, 7.20 (m, 3)	1827 s, 1760 vs (1836 w, 1773 vs)[c]
$Pd(MA)[PPh(t\text{-}Bu)_2]_2$[d] (**16**)	1.32 (d, 18)	11.6	*o*-H, 7.50 (br, 2); *m*- and *p*-H, 6.84 (m, 3) =CH, 3.65 (s, 1)	1790 s, 1725 vs
$Pt(MA)[PPh(t\text{-}Bu)_2]_2$[d] (**17**)	1.22 (d, 9) 1.34 (d, 9)	10.0 11.0	*o*-H, 7.36 (m, 2); *m*- and *p*-H, 6.64 (m, 3) =CH, 3.65 (d, 1); J_{H-P} = 4.4 Hz, J_{H-Pt} = 58.0 Hz	1795 s, 1728 vs
$Pd(DF)_2[PPh(t\text{-}Bu)_2]$[e] (**18**)	1.22 (d, 9)	13.2	*o*-H, 7.60 (m, 1); *m*- and *p*-H, 7.16 (m)[f] =CH, 5.44 (s, 2); CH_3, 3.36 (s, 6)	1705 s
$Pt(DF)_2[PPh(t\text{-}Bu)_2]$[e,g] (**19**)	1.22 (d, 9)	13.9	*o*-H, 7.55 (m, 1); *m*- and *p*-H, 7.10 (m)[f] =CH, 4.39 (dd, 1), J_{H-H} = 8.9 Hz, J_{H-P} = 7.4 Hz J_{H-Pt} = 62.5 Hz 5.21 (dd, 1), J_{H-H} = 8.9 Hz, J_{H-P} = 5.8 Hz J_{H-Pt} = 49.1 Hz CH_3, 3.15 (s, 3) and 3.56 (s, 3)	1710 s

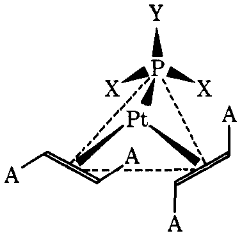
[a] Measured in C_6D_6. Multiplicity and relative intensity are shown in the parentheses. [b] Measured in Nujol mull. [c] In THF. [d] MA = maleic anhydride. [e] DF = dimethyl fumarate. [f] Due to the overlap with the solvent signal, the relative intensity cannot be evaluated. [g] For ^{13}C NMR see Experimental Section.



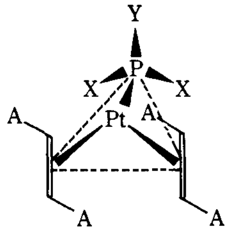
19a



19b



19c



19d

A = CO_2Me, X = *t*-Bu, Y = Ph

olefinic ligands, similar to **19c**, has been established by x-ray analysis for $Ni(CH_2{=}CH_2)_2P(c\text{-}C_6H_{11})_3$.[28] Thus **19c** appears to be a more probable structure.

The formation of **18** and **19** may occur through a dissociative process or an associative one. A limiting mechanism requires either a one-coordinate intermediate $MPPh(t\text{-}Bu)_2$ or a three-coordinate $M(DF)[PPh(t\text{-}Bu)_2]_2$. Support for the latter process is obtained from the temperature-variant ^{1}H NMR of a 1:2.5 mixture of **5** and DF dissolved in toluene-d_8 below −40 °C. At −20 °C the mixture shows a methyl proton signal (δ 3.16, s) of free DF and new signals at δ 4.08 (=CH, 2 H, br s, J_{H-Pt} = 49.6 Hz), 3.45 (CH_3, 6 H, s), 1.64 (*t*-Bu, 18 H, d, J_{H-P} = 12.0 Hz), and 1.08 (*t*-Bu, 18 H, J_{H-P} = 12.0 Hz), the *tert*-butyl proton signal (δ 1.52, t) of **5** observed at −40 °C being completely absent. The two nonequivalent *tert*-butyl and two equivalent olefinic and carbomethoxy proton signals are ascribable to a species, $Pt(DF)[PPh(t\text{-}Bu)_2]_2$. On raising the temperature the signals due to **19** begin to appear at the expense of the resonances due to $Pt(DF)[PPh(t\text{-}Bu)_2]_2$. At 35 °C **19** and $Pt(DF)[PPh(t\text{-}Bu)_2]_2$ exist in a 1:2 molar ratio. However, attempts to isolate the latter were unsuccessful. The steric bulk of DF apparently destabilizes the monoolefin bisphosphine complex, while the less bulky MA ligand forms the corresponding stable $Pt(MA)L_2$ complex.

Oxidative addition of HX (X = Cl, $OCOCF_3$) to two-coordinate complexes, **1**, **2**, and **5**, readily takes place at room temperature in *n*-hexane to give *trans*-$MHXL_2$ (**20**, M = Pd, X = Cl, L = $P(t\text{-}Bu)_3$; **21**, M = Pd, X = Cl, L = $PPh(t\text{-}Bu)_2$; **22**, M = Pd, X = $OCOCF_3$, L = $P(t\text{-}Bu)_3$; **23**, M = Pd, X = $OCOCF_3$, L = $PPh(t\text{-}Bu)_2$; **24**, M = Pt, X = Cl, L = $PPh(t\text{-}Bu)_2$). In view of the extremely large cone angle, the existence of the square planar tetracoordination is rather astonishing. The hydride **20** is also obtained by treating $PdCl_2(PhCN)_2$ with $P(t\text{-}Bu)_3$ in benzene under reflux. The trans configuration is deduced from triplet patterns of the hydride and *tert*-butyl proton signals (Table V).

Remarkably, the Pt(0) complex **7** reacts readily with MeOH (pK_a = 17.7) at room temperature to give *trans*-$PtH_2[P(i\text{-}Pr)_3]_2$ (**25**) in good yield. The three-coordinate complex $Pt[P(i\text{-}Pr)_3]_3$ (**8**) also gives **25** upon treating with MeOH, liberating 1 mol of $P(i\text{-}Pr)_3$. Similarly $Pt[P(c\text{-}C_6H_{11})_3]_2$ (**6**) reacts with MeOH under reflux for 1 h to give *trans*-$Pt(H)_2[P(c\text{-}C_6H_{11})_3]_2$ (**26**). Formation of *trans*-$Pt(H)_2[PPh(t\text{-}Bu)_2]_2$ (**27**) from **5** and MeOH is rather slow, requiring a prolonged refluxing (17 h).

The *trans*-dihydrides **25** and **26** are also obtained by molecular hydrogen addition to **7** and **6** in benzene at room temperature under atmospheric pressure in almost quantitative yield. Similarly H_2 adds to **8** with dissociation of 1 mol of $P(i\text{-}Pr)_3$ to give **25**. The reaction of **6** with D_2 gives the corresponding dideuteride showing ν(Pt-D) at 1230 cm^{-1}; ν(Pt-H)/ν(Pt-D) = 1.39. The two-coordinate triethylphosphine complex $Pt(PEt_3)_2$ prepared from *trans*-$PtCl_2(PEt_3)_2$ and Na/Hg in situ also reacts with H_2 to give *trans*-$PtH_2(PEt_3)_2$ (**28**). H_2 does not add to **4** and **5** under similar conditions.

The *trans*-dihydride complexes are diamagnetic colorless crystals soluble in benzene. In contrast to the poor solubility of **26** and **27** in MeOH and *n*-hexane, **25** and **28** are readily soluble. They are thermally very stable, except for **28**. For example, **25** melts at 59-60 °C without decomposition in air, while **28** decomposes gradually above 25 °C under nitrogen. The thermal stability of *trans*-dihydrides (**25**, **26**, and **27**) is attributable to a kinetic origin, since there is no appreciable

Table V. Spectral Data of Hydride Complexes

	^{1}H NMR[a]						IR, cm^{-1} [b]	
	H–M			CH_3				
	δ, ppm, Me_4Si	$J_{H\text{-}P}$, Hz	$J_{H\text{-}Pt}$, Hz	δ, ppm, Me_4Si	$^3J_{H\text{-}P}$ + $^5J_{H\text{-}P}$, Hz	Other	ν(M–H)	Other
trans-PdH(Cl)[P(*t*-Bu)$_3$]$_2$ (**20**)	−16.5 (t)	6.9		1.51 (t)	12.3		2210	247 (ν(Pd–Cl))
trans-PdH(Cl)[PPh(*t*-Bu)$_2$]$_2$ (21)	−15.1 (t)	6.7		1.45 (t)	12.6	6.8–7.3 (m, *m*- and *p*-H) 8.08 (m, *o*-H)	2063	270 (ν(Pd–Cl))
trans-PdH(OCOCF$_3$)[P(*t*-Bu)$_3$]$_2$ (**22**)	−18.3 (t)	4.3		1.38 (t)	12.5		2190	1690 (ν(CO))
trans-PdH(OCOCF$_3$)[PPh(*t*-Bu)$_2$]$_2$ (**23**)	−17.2 (t)	5.6		1.32 (t)	14.0	7.0–7.3 (m, *m*- and *p*-H) 8.0 (m, *o*-H)	2140	1690 (ν(CO))
trans-PtH(Cl)[PPh(*t*-Bu)$_2$]$_2$ (**24**)	−12.08 (t)	12.4	*c*	1.45 (t)	15.2	7.1–7.4 (m, *m*- and *p*-H) 8.24 (m, *o*-H)	2252	267 (ν(Pt–Cl))
trans-PtH(Cl)[P(*i*-Pr)$_3$]$_2$ (**29**)	−11.66 (t)	12.0	*c*	1.22 (q)[d]	15.2	2.36 (m, CH)	2182	268 (ν(Pt–Cl))
trans-Pt(H)$_2$[P(*i*-Pr)$_3$]$_2$ (**25**)	−3.22 (t)	17.3	790.4	1.24 (q)[e]	15.8	2.06 (m, CH)	1735	
trans-Pt(H)$_2$[P(c-C$_6$H$_{11}$)$_3$]$_2$ (**26**)	−3.05 (t)	17.6	798.0			1.0–2.5 (m, c-C$_6$H$_{11}$)	1710	
trans-Pt(H)$_2$[PPh(*t*-Bu)$_2$]$_2$ (**27**)	−3.05 (t)	16.5	790.8	1.54 (t)	12.8	7.0–7.3 (m, *m*- and *p*-H) 8.58 (m, *o*-H)	1780	
trans-Pt(H)$_2$(PEt$_3$)$_2$ (28)	−2.22 (t)	15.1	792.4	1.06 (br)		1.65 (br, CH$_2$)	1725	

[a] Measured in benzene-d_6. [b] Measured in Nujol mull. [c] Due to the low solubility ^{195}Pt satellites were not detected. [d] 1:3:3:1 quartet, $J_{H\text{-}H}$ = 7.6 Hz. [e] 1:3:3:1 quartet, $J_{H\text{-}H}$ = 7.9 Hz.

difference in $J_{H\text{-}Pt}$ and ν(Pt–H) for a series of *trans*-dihydrides, including the PEt$_3$ analogue **28** (Table V). The IR spectra of the dihydride compounds (Table V) show a very strong Pt–H stretching absorption in a region of 1710–1780 cm^{-1}, which is the region usually found for ν(M–H) of *trans*-dihydrides; e.g., *trans*-$MH_2[C_2H_4(PEt_2)_2]_2$ (M = Ru, 1615 cm^{-1}; M = Os, 1712 cm^{-1}).[29] The hydride proton signals of **25**, **26**, **27**, and **28** are observed at δ −2.22 to −3.22 as triplets with Pt satellites ($J_{H\text{-}Pt}$ = 790–798 Hz). The very low Pt–H stretching frequencies and the enormous deshielding of hydride protons [cf. *trans*-PtH(η^1-cyclohexenyl)(PPh$_3$)$_2$,[30] ν(Pt–H) = 1920 cm^{-1}, δ (ppm, Me$_4$Si) −4.64 (Pt–H)] are ascribed to the strong trans influence of the hydride in mutually trans positions.

25 and **27** react with excess CHCl$_3$ at 60 °C to give *trans*-PtHClL$_2$ (**29**, L = P(*i*-Pr)$_3$; **24**, L = PPh(*t*-Bu)$_2$). The strong Pt–H bonding in **29** and **24** is reflected in the high Pt–H stretching frequency and the strong shielding of the hydride proton as compared with the corresponding value of the *trans*-dihydride (Table V).

The addition of MeOH to give stable *trans*-dihydride is notable since to our knowledge, no other Pt(0) is known to react with alcohol except for Pt(PEt$_3$)$_3$, which was reported to form unisolable [PtH(PEt$_3$)$_3$]OCH$_3$.[31] Formation of *trans*-dihydrides from reaction with MeOH apparently takes place through an oxidative addition of MeOH followed by β-hydrogen elimination from the methoxy complex PtH(OCH$_3$)(PR$_3$)$_2$ produced. In fact, aldehyde can be isolated from a reaction of PtL$_2$ with alcohol. For example, heating a mixture of benzyl alcohol and **7** in toluene we obtained 4.5 mol of benzaldehyde/mol of the complex. Pt(PEt$_3$)$_3$[31,32] shows high dehydrogenation activity compared to **7**, while Pd(PEt$_3$)[32] is less efficient, producing only 2 mol of benzaldehyde/mol of the complex.

The complex **1** fails to react with *p*-cresol (pK_a = 10.2) in *n*-hexane under reflux for 10 h. Similarly **1**, **2**, and **3** are inert toward hydrogen even under 100 kg/cm^2 pressure at 60–70 °C. The insensitivity of PdL$_2$ toward H$_2$ is in marked contrast to the high reactivity of the Pt analogues. However, **2** absorbs H$_2$ on irradiation with a low-pressure Hg lamp under normal pressure to produce a hydride complex as a dark brown solid showing ν(Pd–H) and δ(Pd–H) at 2260 and 847 cm^{-1}, respectively. Purification and characterization of this polynuclear hydride has been unsuccessful due to its insolubility.

The properties of both the phosphine ligand and the metal identity affect the oxidative addition of H$_2$ and MeOH. Qualitatively, the reactivity of Pt(0) phosphine complexes toward H$_2$ and MeOH appears to increase in the order, P(*t*-Bu)$_3$ ≪ PPh(*t*-Bu)$_2$ < P(c-C$_6$H$_{11}$)$_3$ < P(*i*-Pr)$_3$. As the cone angle[3] of the phosphines employed increases in the order P(*i*-Pr)$_3$ (160 ± 10°) < P(c-C$_6$H$_{11}$)$_3$ (179 ± 10°) ≲ PPh(*t*-Bu)$_2$ (170 ± 2°) < P(*t*-Bu)$_3$ (182 ± 2°), the reactivity of two-coordinate Pt(0) complexes may be primarily governed by the steric size of the phosphine. However, since **5** adds O$_2$ and MeOH, more bulky molecules than H$_2$, the reluctance of **5** to undergo oxidative addition suggests the importance of the electronic property of phosphine. The basicity of the phosphines[33] increases in the order PPh(*t*-Bu)$_2$ < P(*i*-Pr)$_3$ < P(c-C$_6$H$_{11}$)$_3$ < P(*t*-Bu)$_3$. In contrast to the Pt(0) complexes, the inertness of the corresponding Pd(0) complexes **1**, **2**, and **3** toward H$_2$ and MeOH may be ascribed to the low basicity of palladium metal. The ionization potentials[34] are 8.20 and 8.33 eV for Pt(0) and Pd(0), respectively. The difference in basicity between two metals is also manifested in ν(CO) of M$_3$(CO)$_3$[PPh(*t*-Bu)$_2$]$_3$ (M = Pd, 1872, 1823; Pt, 1836, 1773 cm^{-1}) and of M(CO)(PEt$_3$)$_3$ (M = Pd, 1944; Pt, 1920 cm^{-1}).[35] A similar trend has been observed for the addition of H$_2$ to $[M(Ph_2PCH_2CH_2PPh_2)_2]^+$ [36] (M = Rh, Ir); the Ir(I) complex gives readily the dihydride complex, while Rh(I) complex does not.

Uchida et al.[37] have reported that *trans*-PtH$_2$[P(c-C$_6$H$_{11}$)$_3$]$_2$ was obtained by the reduction of Pt(acac)$_2$ with AlR$_3$ in the presence of P(c-C$_6$H$_{11}$)$_3$. The ν(Pt–H) (1910 cm^{-1}) differs from ours and the reported insolubility, preventing ^{1}H NMR measurement, contradicts our observation. Recently three other groups[38-40] reported preparation of **26** with spectral data which agree with ours.

An attempt to isolate a hydrido-hydroxo complex PtH(OH)[PPh(*t*-Bu)$_2$] by oxidative addition of H$_2$O to **5** under reflux in xylene was fruitless, **5** being recovered almost quantitatively. However, the formation of hydrido-hydroxo complex as a transient species is evident from a catalysis by **5** of the hydration of nitriles and the H–D exchange reaction of PhCOCH$_3$ with D$_2$O. The details will be published separately.

Experimental Section

Preparation of ML$_2$ complexes (M = Pd, L = P(*t*-Bu)$_3$, PPh(*t*-Bu)$_2$, P(c-C$_6$H$_{11}$)$_3$; M = Pt, L = P(*t*-Bu)$_3$, PPh(*t*-Bu)$_2$, P(c-C$_6$H$_{11}$)$_3$, P(*i*-Pr)$_3$) and Pt[P(*i*-Pr)$_3$]$_3$ were described previously.[2] The ^{13}C NMR was obtained using a JNM FX100 Fourier transform spectrometer. Other spectroscopic data were recorded on the same instruments as

Table VI. Physical and Analytical Data

	Color	Mp, °C	Anal[a]	
			C	H
$PdO_2[PPh(t\text{-}Bu)_2]_2C_6H_5CH_3$	Green	102–105 dec	62.3 (62.3)	8.3 (8.7)
$PdO_2[P(c\text{-}C_6H_{11})_3]_2$	Green	104–105 dec	62.8 (61.8)	9.8 (9.5)
$PtO_2[PPh(t\text{-}Bu)_2]_2$	Pale brown	150–152 dec	49.8 (50.0)	6.8 (6.9)
$PtO_2[P(c\text{-}C_6H_{11})_3]_2$	Pale brown	133-135 dec	55.2 (54.9)	8.6 (8.4)
$Pd_3(CO)_3[P(t\text{-}Bu)_3]_3$	Yellow	99-102 dec	46.7 (46.3)	8.2 (8.1)
$Pd_3(CO)_3[PPh(t\text{-}Bu)_2]_3$[b]	Yellow	95.7 dec	50.8 (5.05)	6.7 (6.5)
$Pt_3(CO)_3[PPh(t\text{-}Bu)_2]_3$	Orange red	185–190 dec	40.7 (40.5)	6.3 (5.2)
$Pd(MA)[PPh(t\text{-}Bu)_2]_2$[d]	Yellow	108–112 dec	59.0 (59.2)	7.3 (7.5)
$Pt(MA)[PPh(t\text{-}Bu)_2]_2$[d]	Colorless	134–135 dec	51.4 (52.1)	6.5 (6.6)
$Pd(DF)_2[PPh(t\text{-}Bu)_2]$[e]	Colorless	104-108 dec	50.6 (50.6)	6.4 (6.4)
$Pt(DF)_2[PPh(t\text{-}Bu)_2]$[e]	Colorless	126-129 dec	44.2 (44.2)	5.7 (5.6)
trans-$PdH(Cl)[P(t\text{-}Bu)_3]_2$[f]	Colorless	144–147 dec	52.4 (52.6)	10.0 (10.1)
trans-$PdH(Cl)[PPh(t\text{-}Bu)_2]_2$	Colorless	128–130 dec	57.2 (57.3)	8.0 (8.1)
trans-$PdH(OCOCF_3)[P(t\text{-}Bu)_3]_2$	Pale yellow	97-101 dec	50.0 (50.0)	9.0 (9.0)
trans-$PdH(OCOCF_3)[PPh(t\text{-}Bu)_2]_2$	Colorless	97-99 dec	54.2 (54.2)	7.2 (7.1)
trans-$PtH(Cl)[PPh(t\text{-}Bu)_2]_2$[g]	Colorless	223-224 dec	49.7 (49.7)	7.0 (7.1)
trans-$PtH(Cl)[P(i\text{-}Pr)_3]_2$[h]	Colorless	137–141	39.0 (39.2)	7.8 (7.9)
trans-$Pt(H)_2[PPh(t\text{-}Bu)_2]_2$	Colorless	158–169 dec	52.1 (52.4)	7.4 (7.5)
trans-$Pt(H)_2[P(c\text{-}C_6H_{11})_3]_2$[i]	Colorless	158–159 dec	56.7 (57.0)	9.2 (9.0)
trans-$Pt(H)_2[P(i\text{-}Pr)_3]_2$	Colorless	59-60	41.9 (41.8)	8.7 (8.6)

[a] Calculated values are shown in the parentheses. [b] Mol wt: calcd, 1068; found,[c] 950. [c] Measured cryoscopically in benzene. [d] MA = maleic anhydride. [e] DF = dimethyl fumarate. [f] %Cl: calcd, 6.48; found, 6.54. [g] %Cl: calcd, 5.25; found, 5.18. [h] %Cl: calcd, 6.43; found, 6.62. [i] Mol wt: calcd, 757; found, 708.

before.[2] All reactions and physical measurements were carried out in a nitrogen atmosphere. Physical and analytical data of the new compounds obtained are listed in Table VI.

I. Kinetic Measurement. ^1H NMR spectra were measured in benzene or anisole solution containing toluene (5%). For a system of $Pd[PPh(t\text{-}Bu)_2]_2$ and $PPh(t\text{-}Bu)_2$ the line widths of the *tert*-butyl proton signals were calibrated with that of the methyl proton signal of toluene. No calibration could be made for the Pt complex due to the high temperature. Below the coalescence temperature the line width of each peak of the triplet due to **2** and that of each peak of the doublet due to free $PPh(t\text{-}Bu)_2$ are related to the average lifetime τ_c of a phosphine molecule in **2** and the average lifetime τ_f of free $PPh(t\text{-}Bu)_2$, respectively. The relation is expressed as follows,[41] $W_c = W_c^o + (\pi\tau_c)^{-1}$ and $W_f = W_f^o + (\pi\tau_f)^{-1}$, where W^o is the observed line width in the absence of exchange. The rate law for the ligand exchange reaction was obtained at 63 °C from the spectra of the following solutions in benzene (C, concentration of complex; L, concentration of free phosphine): $C = 8.2 \times 10^{-2}$, $L = 1.5 \times 10^{-1}$ M; $C = 8.2 \times 10^{-2}$, $L = 1.1 \times 10^{-1}$ M; $C = 8.2 \times 10^{-2}$, $L = 7.3 \times 10^{-2}$ M; $C = 8.2 \times 10^{-2}$, $L = 3.9 \times 10^{-2}$ M; $C = 1.4 \times 10^{-1}$, $L = 2.0 \times 10^{-1}$ M; $C = 2.5 \times 10^{-1}$, $L = 2.0 \times 10^{-1}$ M. Rate constants of the ligand exchange were evaluated from the line width of the doublet resonance due to free $PPh(t\text{-}Bu)_2$. The higher field line of the doublet was employed for the line width measurement. The rate constants $k\,(s^{-1}\,M^{-1})$ for a system of $Pd[PPh(t\text{-}Bu)_2]_2$ (0.17 M) and $PPh(t\text{-}Bu)_2$ (0.59 M) were 0.03 (35 °C), 0.06 (50 °C), and 0.14 (80 °C). The corresponding values for $Pt[PPh(t\text{-}Bu)_2]_2$ (0.09 M) and $PPh(t\text{-}Bu)_2$ (0.57 M) were 0.27 (110 °C), 0.68 (130 °C), 0.82 (140 °C), and 1.23 (150 °C).

II. Reactions of Two-Coordinate Complexes. 1. With Dioxygen. $Pd(O_2)[PPh(t\text{-}Bu)_2]_2$ (9). Dioxygen was introduced into a solution of **2** (0.28 g, 0.52 mmol) in *n*-hexane (10 mL) at −30 °C under normal pressure. Immediately O_2 absorption took place with precipitation of pale yellowish green needles. the needles were washed with *n*-hexane, dried in vacuo, and recrystallized from toluene to give $Pd(O_2)[PPh(t\text{-}Bu)_2]_2C_6H_5CH_3$ as green crystals. Solid **2** also reacted with O_2 to give **9**. Similarly $Pd(O_2)[P(c\text{-}C_6H_{11})_3]_2$ (**10**), $Pt(O_2)[PPh(t\text{-}Bu)_2]_2$ (**11**), and $Pt(O_2)[P(c\text{-}C_6H_{11})_3]_2$ (**12**) were obtained quantitatively from the corresponding two-coordinate complexes and O_2.

Under similar conditions the solution of **1** (0.51 g, 1 mmol) in *n*-hexane (20 mL) did not react with dioxygen. However, at room temperature the mixture slowly adsorbed 42 mL of dioxygen (48 h) to give a red solution. Concentration in vacuo gave dark red oil, from which a small amount of red crystals was separated. Recrystallization from toluene gave brick red crystals (11 mg, 3%), mp 145-148 °C dec: ^1H NMR (C_6H_6) δ 2.39 (d, 1 H, $J = 12.4$ Hz), 2.02 (d, 1 H, $J = 12.4$ Hz), 1.40–1.90 (m, 11 H), and 1.24 (d, 1 H, $J = 12.0$ Hz).

Anal. Calcd for $C_{12}H_{27}OPPd$: C, 44.38; H, 8.38. Found: C, 44.26; H, 7.96.

Reversibility of the Dioxygen Complexes. A solution of **9** (0.12 g, 0.2 mmol) in MeOH (10 mL) was heated at 60 °C for 2 h. The green solution turned to brown and a yellow crystalline compound separated. Recrystallization of the crystals from *n*-hexane gave **2** (0.07 g, 64%). Alternatively, the crystals of **9** were heated at 60-70 °C under high vacuum (10^{-3} mmHg) for 38 h to give **2**, as determined by the complete disappearance of ν(O-O) (915 cm^{-1}).

Similar treatments of **11** did not cause dissociation of the coordinated dioxygen.

2. With Carbon Monoxide. $Pd_3(CO)_3[P(t\text{-}Bu)_3]_3$ (13). To a solution of **1** (0.15 g, 0.3 mmol) in *n*-hexane (10 mL) CO was bubbled at room temperature. The colorless solution turned yellowish orange and yellow crystals gradually separated. After 1 h, the crystals were filtered, washed with *n*-hexane, and dried in vacuo (0.06 g, 60%). Similarly $Pd_3(CO)_3[PPh(t\text{-}Bu)_2]_3$ (**14**) (85%) and $Pt_3(CO)_3[PPh(t\text{-}Bu)_2]_3$ (**15**) (90%) were obtained from **2** and **5**, respectively.

3. With Olefins. $M(MA)[PPh(t\text{-}Bu)_2]_2$ (16, M = Pd; 17, M = Pt; MA = maleic anhydride). A mixture of **2** (0.11 g, 0.2 mmol) and MA (0.02 g, 0.2 mmol) in *n*-hexane (5 mL) was stirred at 35-40 °C for 2 h. The yellowish orange crystals which separated were filtered, washed with *n*-hexane, and recrystallized from a toluene-*n*-hexane mixture to give **16** quantitatively as yellow crystals. Similarly a reaction of **5** with MA gave **17** quantitatively as colorless crystals.

$M(DF)_2PPh(t\text{-}Bu)_2$ (18, M = Pd; 19, M = Pt; DF = dimethyl fumarate). A mixture of **2** (0.11 g, 0.2 mmol) and DF (0.03 g, 0.2 mmol) in *n*-hexane (7 mL) was stirred at 30-40 °C for 2 h. The mixture, after concentration in vacuo, gave the starting materials. Separately the mixture of **2** and DF in the same mole ratio in toluene (7 mL) was heated at 70-80 °C for 17 h. Concentration to 0.5 mL, followed by an addition of *n*-hexane (4 mL), gave **18** as colorless crystals (32%). A similar reaction of **5** with 2 mol of DF at 70-80 °C for 17 h gave **19** as colorless crystals (64%). ^{13}C NMR (benzene-d_6, δ(ppm) from Me_4Si) of **19**: $=CH-$, δ 55.7 (d, $J_{C-P} = 10.6$, $J_{C-Pt} = 212.2$ Hz) and 56.2 (d, $J_{C-P} = 12.0$, $J_{C-Pt} = 133.0$ Hz); $C=O$, 168.0 (d, $J_{C-P} = 2.4$, $J_{C-Pt} = 38.4$ Hz) and 170.1 (s, $J_{C-P} = 0$, $J_{C-PPt} = 38.0$ Hz); CH_3O, 50.8 (s) and 51.8 (s); $\geqslant C-P$, 36.8 (d, $J_{C-P} = 19.3$, $J_{C-Pt} = 36.0$ Hz) and 36.9 (d, $J_{C-P} = 19.3$, $J_{C-Pt} = 36.0$ Hz); CH_3, 29.8 (d, $J_{C-P} = 15.6$ Hz) and 30.2 (d, $J_{C-P} = 15.6$ Hz).

4. With Protic Acids. *trans*-$PtH(Cl)[P(t\text{-}Bu)_3]_2$ (20). To a solution of **1** (0.10 g, 0.2 mmol) in *n*-hexane (10 mL) was added a 0.33 N benzene solution of HCl (0.61 mL) at room temperature. Colorless crystals which precipitated were filtered, washed with *n*-hexane, and dried in vacuo to give **20** quantitatively. Alternatively **20** was obtained directly by heating a mixture of $\mathrm{Pd(PhCN)_2Cl_2}$ (0.38 g, 1 mmol) and $\mathrm{P(}t\mathrm{\text{-}Bu)_3}$ (0.60 g, 3 mmol) in benzene at 80 °C for 2 h (32%).

Similarly *trans*-$\mathrm{MH(Cl)[PPh(}t\mathrm{\text{-}Bu)_2]_2}$ (**21**, M = Pd; **24**, M = Pt) and *trans*-$\mathrm{PdH(OCOCF_3)L_2}$ (**22**, L = $\mathrm{P(}t\mathrm{\text{-}Bu)_3}$; **23**, L = $\mathrm{PPh(}t\mathrm{\text{-}Bu)_2}$) were obtained almost quantitatively from the corresponding two-coordinate complexes and a stoichiometric amount of HX (X = Cl, $\mathrm{OCOCF_3}$).

5. With Alcohols. *trans*-$\mathrm{Pt(H)_2L_2}$ (25, L = $\mathrm{P(}i\mathrm{\text{-}Pr)_3}$; 26, L = $\mathrm{P(c\text{-}C_6H_{11})_3}$; 27, L = $\mathrm{PPh(}t\mathrm{\text{-}Bu)_2}$). A THF solution of **7** prepared by treating *trans*-$\mathrm{PtCl_2[P(}i\mathrm{\text{-}Pr)_3]_2}$ (0.58 g, 1 mmol) with 1% Na/Hg (23 g) was evaporated to dryness and the crude **7** was added to 5 mL of MeOH at room temperature. The reddish purple oil was dissolved immediately to give a pale brown solution which upon concentration in vacuo gave colorless crystals. Washing with MeOH at −40 °C and subsequent recrystallization from *n*-hexane gave **25** (0.28 g, 54%). Similarly a reaction of **8** with MeOH at room temperature gave **25** (70%).

Similar treatment of **5** and **6** with MeOH under gentle reflux (17 h for **5** and 1 h for **6**) gave **27** (70%) and **26** (79%), respectively. **2** and **3** failed to react with MeOH (under reflux for 15 h). **1** was recovered quantitatively after heating (75–80 °C, 10 h) with *p*-cresol.

Dehydrogenation of Benzyl Alcohol. A mixture of **7** (0.051 g, 0.1 mmol) and benzyl alcohol (1.20 g) in toluene (5 mL) was heated under gentle reflux for 21 h. VPC analysis (PEG 20 m, 180 °C) of the reaction mixture showed formation of 4.5 mol of benzaldehyde/mol of **7**. Under similar conditions but employing $\mathrm{Pt(PEt_3)_3}$ and $\mathrm{Pd(PEt_3)_3}$ as catalyst, 21.6 and 2.2 mol of benzaldehyde were obtained per mole of catalyst, respectively.

6. With Molecular Hydrogen. *trans*-$\mathrm{Pt(H)_2L_2}$ (25, L = $\mathrm{P(}i\mathrm{\text{-}Pr)_3}$; 26, L = $\mathrm{P(c\text{-}C_6H_{11})_3}$). To a benzene-$d_6$ solution of **7** or **6** in a NMR tube was bubbled $\mathrm{H_2}$ at room temperature for 5 min. The ^{1}H NMR spectrum of the reaction mixture was completely identical with those of the corresponding *trans*-dihydrides. Similarly the ^{1}H NMR spectrum of the reaction mixture of **8** with $\mathrm{H_2}$ at room temperature showed the formation of **25** with a dissociation of 1 mol of $\mathrm{P(}i\mathrm{\text{-}Pr)_3}$. Similar reaction of **6** with $\mathrm{D_2}$ gave colorless solid *trans*-$\mathrm{Pt(D)_2[P(c\text{-}C_6H_{11})_3]_2}$ (ν(Pt–D) 1230 cm^{-1}).

Under comparable conditions **4** and **5** were inert toward $\mathrm{H_2}$. Similarly Pd complexes **1**, **2**, and **3** failed to react with $\mathrm{H_2}$ (100 kg/cm^2) at 60–70 °C in benzene.

***trans*-$\mathrm{Pt(H)_2(PEt_3)_2}$ (28).** A mixture of *trans*-$\mathrm{PtCl_2(PEt_3)_2}$ (0.50 g, 1 mmol) and 1% Na/Hg (23 g) in THF (10 mL) was stirred at room temperature for 5 h under $\mathrm{H_2}$ (1 atm). About 21 mL of $\mathrm{H_2}$ was absorbed. After filtration under $\mathrm{H_2}$, the pale brown solution was concentrated in vacuo to give colorless crystals contaminated with dark brown oil. Recrystallization from *n*-hexane at −70 °C gave colorless crystals (0.23 g, 53%). The dihydride decomposed gradually above room temperature and an analytically pure sample was not obtained. However, its formation is evident from ^{1}H NMR and IR spectra (Table V).

Reaction of $\mathrm{Pd[PPh(}t\mathrm{\text{-}Bu)_2]_2}$ (2) with $\mathrm{H_2}$ under Irradiation. A *n*-hexane solution of **2** (0.153 g, 0.3 mmol) was irradiated with a low-pressure Hg lamp at 0 °C under $\mathrm{H_2}$ (1 atm) for 6 h. The colorless solution turned into dark brown and the brown amorphous solids were deposited with absorption of $\mathrm{H_2}$ (ca. 5 mL). The IR spectrum showed ν(Pd–H) and δ(Pd–H) at 2260 and 847 cm^{-1}, respectively. Attempted purification was unsuccessful.

III. Miscellaneous. Reaction of *trans*-$\mathrm{Pt(H)_2(PR_3)_2}$ (25 and 27) with $\mathrm{CHCl_3}$. A mixture of **25** (0.105 g, 0.2 mmol) and $\mathrm{CHCl_3}$ (0.5 ml) in *n*-hexane (5 mL) was heated at 60 °C for 0.5 h. The concentrated reaction mixture was recrystallized from toluene to give *trans*-$\mathrm{PtH(Cl)[P(}i\mathrm{\text{-}Pr)_3]_2}$ (**29**) (0.073 g, 66%). A similar reaction of **27** with $\mathrm{CHCl_3}$ gave **24** (59%).

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