Triarylphosphine and Ethylene Complexes of Zerovalent Nickel, Palladium, and Platinum

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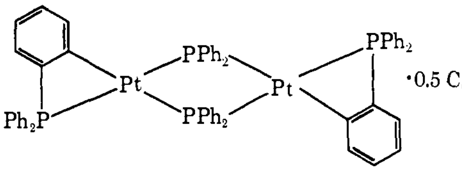
Abstract: Physical studies on solutions of zerovalent nickel, palladium, and platinum complexes containing ethylene and arylphosphine ligands ($L = P(C_6H_5)_3$, $P(p\text{-}C_6H_4CH_3)_3$, or $P(m\text{-}C_6H_4CH_3)_3$) are reported. The ML_4 complexes are substantially dissociated into ML_3 and L at 25°; the PtL_4 complexes have, however, been detected by ^{31}P nmr at −90°. No dissociation of ML_3 or $(C_2H_4)ML_2$ complexes was detected. Equilibrium constants in benzene at 25° are reported for $ML_3 + C_2H_4 \rightleftharpoons (C_2H_4)ML_2 + L$ and found to be 300, 0.12, and 0.013 for M = Ni, Pt, and Pd ($L = P(C_6H_5)_3$). The results are discussed in terms of electronic and steric effects.

More than 10 years ago Malatesta and coworkers reported the preparation of triarylphosphine complexes of Pd(0)[2a] and Pt(0).[2b] $Ni[PPh_3]_4$[3] and $Ni[PPh_3]_2$[3] were reported in 1961, but the latter was soon shown to be $(C_2H_4)Ni[PPh_3]_2$.[4] Preparations of $(C_2H_4)Pt[PPh_3]_2$[5] and $(C_2H_4)Pd[PPh_3]_2$[5c] appeared more recently. Although many of these compounds have been known for some time, the nature of the species present in solution has remained obscure. Malatesta and Cariello[2] isolated both tetrakis and tris complexes of Pt with triphenylphosphine, but only a tris complex with tri(*p*-chlorophenyl)phosphine. Cryoscopic molecular weights on $Pt[PPh_3]_4$ and $Pt[PPh_3]_3$ were so low that both compounds were said to dissociate extensively in solution to the bis complex $Pt[PPh_3]_2$. Equilibrium constants for dissociation of $Pt[PPh_3]_3$[6] and $(C_2H_4)Pt[PPh_3]_2$[7] to $Pt[PPh_3]_2$ have been reported based on an analysis of kinetic data. $Pt[PPh_3]_2$ has been proposed as an intermediate in exchange reactions of (acetylene)$Pt[PPh_3]_2$ complexes[8] and is said to have been isolated as an unstable solid.[9] The picture is complicated by the existence of cluster compounds of platinum[10] thought to be $[PtPPh_3]_4$ and $[Pt(PPh_3)_2]_3$. Furthermore, attempts to prepare $Pt[PPh_3]_2$ by the uv irradiation of bis(triphenyophosphine)platinum oxalate gave products characterized as **1**[11] or as a stable dimer $[Pt(PPh_3)_2]_2$.[12] X-Ray crystal structures have been determined for $Pt[PPh_3]_3$,[13] $(C_2H_4)Pt[PPh_3]_2$,[14] and $(C_2H_4)Ni[PPh_3]_2$.[14–16]



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The nature of the species present in solutions of these zerovalent metal complexes is important in understanding the kinetics of their reactions. There has been particular interest recently in oxidative-addition reactions.[17] Review articles on phosphine[18] and olefin and acetylene[19] complexes of nickel, palladium, and platinum have appeared.

We wish to report physical studies characterizing the various species present in solutions containing ML_4, ML_3, and $(C_2H_4)ML_2$, where L is a triarylphosphine and M is zerovalent Ni, Pd, or Pt. A combination of experimental techniques has been employed, including molecular weight determinations, ^{31}P and ^1H nmr spectra, and electronic spectra. Equilibrium constants K_1 have been measured in benzene at 25° for the reaction

$$ML_3 + C_2H_4 \rightleftharpoons (C_2H_4)ML_2 + L \qquad (1)$$

and limits set on equilibrium constants for the reactions

$$ML_4 \rightleftharpoons ML_3 + L \qquad (2)$$

$$ML_3 \rightleftharpoons ML_2 + L \qquad (3)$$

$$(C_2H_4)ML_2 \rightleftharpoons ML_2 + C_2H_4 \qquad (4)$$

Experimental Section

Because all the compounds involved in this work are sensitive to oxygen to some degree, all were prepared and handled under N_2. Special precautions were necessary for spectrophotometric work with dilute solutions. For these experiments, solutions were prepared in a Vacuum Atmospheres, Inc. HE-43-2 drybox under condi-

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(1) Joint contribution of CRD and Plastics Departments.

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(3) (a) G. Wilke, E. W. Müller, and M. Kröner, *Angew. Chem.*, **73**, 33 (1961); (b) PPh_3 is used here and subsequently as an abbreviation for $P(C_6H_5)_3$.

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Table I. Determination of K_1 for Additions of C_2H_4 Gas to 1 ml of 2.39×10^{-3} *M* $Pt[PPh_3]_3$ in Benzene at 25° [a]

Added C_2H_4, cm^3	$[C_2H_4]_{tot}$[b]	$10^3[C_2H_4]$[f]	$A(332)$[c]	$10^3[PtL_3]$[d]	$10^3[(C_2H_4)PtL_2]$[e]	K_1[g]
None	0.00	0.00	0.71	2.39	0.00	
0.03	0.00123	0.50	0.62	2.04	0.35	0.120
0.10	0.0041	2.0	0.54	1.74	0.65	0.121
0.30	0.0123	6.4	0.44	1.35	1.04	0.125
1.0	0.041	22.5	0.31	0.85	1.54	0.124
3.0	0.123	69	0.205	0.44	1.95	0.125
6.0	0.246	139	0.16	0.27	2.12	0.120
		∞	(0.09)[h]	0.00	2.39	
						0.122 ± 0.003

[a] 0.1-mm cell. Total cell volume, 3.48 cm^3. [b] $[C_2H_4]_{tot}$ = cm^3 of $C_2H_4/24.4$. [c] Absorbance at 332 mμ. [d] $[PtL_3] = (2.39 \times 10^{-3})(A - A_\infty)/(0.71 - A_\infty)$. [e] $[(C_2H_4)PtL_2] = 2.39 \times 10^{-3} - [PtL_3]$. [f] $[C_2H_4] = 0.57\{[C_2H_4]_{tot} - [(C_2H_4)PtL_2]\}$. [g] $K_1 = [(C_2H_4)PtL_2][L]/[PtL_3] \cdot [C_2H_4] = [(C_2H_4)PtL_2]^2/[PtL_3][C_2H_4]$. [h] A_∞ was determined by successive approximation so as to minimize the deviations of the individual calculated K_1's from the mean.

tions where 1.5 *M* diethylzinc in heptane did not smoke (less than 5 ppm of O_2). The reagent grade benzene solvent was deoxygenated by vigorously purging N_2 for 5 min in the drybox after an initial 5-min purge in air. With these precautions we have been able to obtain good Beer's law behavior on solutions of highly O_2-sensitive compounds down to 10^{-4} *M* complex. At 10^{-5} *M* complex, deviations have been observed which can be attributed to reaction of traces of O_2. Reaction with O_2, rather than reversible ligand dissociation, can be verified by adding ligand to suppress any ligand dissociation which may occur. .

Electronic spectra were recorded from 700 to 270 mμ with a Cary 14 spectrophotometer whose cell compartment was thermostated at 25.0°, using serum-capped quartz cells. Beer's law in benzene was checked by running spectra of 10^{-2}, 10^{-3}, and 10^{-4} *M* complex in cells of 0.1-, 1.0-, and 10-mm length, keeping the product of concentration and path length constant. The effect of added ligand on the spectra was determined in a 0.1-mm cell with solutions containing 2.5×10^{-3} *M* metal complex and 0.5 *M* $P(p\text{-}C_6H_4CH_3)_3$ or $P(m\text{-}C_6H_4CH_3)_3$ or 1 *M* PPh_3 (which was more soluble).

Equilibrium constants for ethylene complex formation were determined by adding increments of C_2H_4 gas with a precision gas syringe from Precision Sampling Corp. to a serum-capped 0.1-mm cell (3.48 cm^3 total volume) containing a 1.0-ml solution of metal complex at a concentration of 2.0 to 7.0×10^{-3} *M*. Before these additions, the partial pressure in the cell was reduced by withdrawing 1 cm^3 of N_2 gas. After each C_2H_4 addition, the cell was thoroughly shaken to ensure equilibrium of the gas between liquid and vapor phases. The total concentration of C_2H_4 in solution was determined assuming that ethylene behaved as a perfect gas, with a molar volume of 24.4 l. at 25° and 1 atm. The actual concentration was found after correcting for the ethylene in the complex and the distribution between liquid and vapor phases. The solubility of ethylene in benzene at 25° was taken to be 3.3 cm^3/cm^3.[20] A sample calculation involving the reaction of C_2H_4 with $Pt[PPh_3]_3$ is shown in Table I.

Molecular weights were determined cryoscopically in N_2-blanketed benzene on solutions about 0.015 *M* in complex using a Hewlett-Packard quartz crystal thermometer as described by Fok, Robson, and Youngken.[21] Proton nmr spectra were recorded in C_6D_6 at ambient temperature (~25°) on a Varian HA-100 using internal tetramethylsilane (TMS) as a reference. ^{31}P nmr spectra were recorded in toluene or a 50/50 mixture of toluene and CH_2Cl_2 on Varian HA-100 (40.5 MHz) or Bruker HFX-90 (36.43 MHz) spectrometers. Chemical shifts were measured with respect to 85% H_3PO_4. Melting points were determined in sealed evacuated tubes and are uncorrected.

Attempts to Remove C_2H_4 from $(C_2H_4)Pt[PPh_3]_2$ and $(C_2H_4)Ni[PPh_3]_2$ under Vacuum. To 0.1 mmol of a $(C_2H_4)M[PPh_3]_2$ complex was added 2 ml of benzene. The solution was vigorously stirred magnetically and a vacuum applied with a vacuum pump and liquid N_2 trap. Pumping was continued for 0.5 hr after the solvent had been removed. The remaining solid from the nickel complex was black, while that from the platinum was light brown. Each of the residues was washed with 0.5 ml of C_6D_6 containing TMS, and the resulting solutions were filtered to remove insoluble solids. The proton nmr spectra of the resulting solutions were essentially identical[22] with those of the initial ethylene complexes, indicating that ethylene was not removed by this treatment. Partial decomposition occurred, but it was irreversible and did not correspond to reversible formation of ML_2 by dissociation of C_2H_4. Bubbling ethylene into the dark brown Ni solution or the light red-brown Pt solution had no effect on the colors of the solutions.

Compounds. The new compounds of platinum and palladium were prepared by the method developed by Coulson[23] for $Pd[PPh_3]_4$.

Tris(tri-*p*-tolylphosphine)palladium.[2a] $Pd[P(p\text{-}C_6H_4CH_3)_3]_3$ was prepared by heating 7.5 g of $P(p\text{-}C_6H_4CH_3)_3$ and 0.875 g of $PdCl_2$ in 40 ml of dimethyl sulfoxide (DMSO) to dissolution (~150°). The solution was allowed to cool to 120° and a 1-ml hydrazine hydrate was added rapidly from a hypodermic syringe. The solution immediately turned dark orange and nitrogen evolved vigorously. When the mixture reached room temperature, 20 ml of absolute ethanol was added and the yellow solid collected. Recrystallization from benzene-methanol afforded 3.4 g (68%) of pure product, mp 215–216°.[24]

Anal. Cald for $Pd[P(C_7H_7)_3]_3$: C, 74.22; H, 6.22; P, 9.11; Pd, 10.43. Found: C, 73.90, 74.02; H, 6.20, 6.23; P, 9.55; Pd, 9.55; Pd, 10.15, 9.91.

Tris(tri-*m*-tolylphosphine)palladium. $Pd[P(m\text{-}C_6H_4CH_3)_3]_3$ was prepared by the hydrazine reduction procedure and isolated as yellow crystals, mp 140–141°.

Anal. Calcd for $Pd[P(C_7H_7)_3]_3$: C, 74.22; H, 6.22; P, 9.11; Pd, 10.43. Found: C, 73.81, 73.90; H, 6.06, 6.03; P, 8.96; Pd, 10.65.

Tris(tri-*p*-tolylphosphine)platinum. $Pt[P(p\text{-}C_6H_4CH_3)_3]_3$ was prepared by heating 12.2 g of $P(p\text{-}C_6H_4CH_3)_3$ and 2.13 g of $PtCl_2$ in 50 ml of DMSO to dissolution (~140°). Cooling to 130° and rapidly adding 1.75 ml of hydrazine hydrate caused vigorous nitrogen evolution and a color change to orange. Quick cooling to 100° precipitated a light orange solid. At room temperature, 20 ml of absolute ethanol was added and the orange solid collected and washed with ethanol and ether. Recrystallization from benzene-methanol produced 6.5 g (73%) of a microcrystalline orange-yellow solid, mp 210–212°.

Anal. Calcd for $Pt[P(C_7H_7)_3]_3$: C, 68.27; H, 5.73; P, 8.38; Pt, 17.60. Found: C, 68.12, 68.52; H, 5.82, 5.83; P, 8.75; Pt, 17.72.

Tris(tri-*m*-tolylphosphine)platinum. $Pt[P(m\text{-}C_6H_4CH_3)_3]_3$ was synthesized using the hydrazine reduction described above and isolated as yellow-orange crystals from benzene-methanol (65%), mp 148–149°.

Anal. Calcd for $Pt[P(C_7H_7)_3]_3$: C, 68.27; H, 5.73; P, 8.38; Pt, 17.60. Found: C, 68.51, 68.22; H, 5.83, 5.68; P, 8.27; Pt, 17.75.

Tetrakis(tri-*m*-tolylphosphine)platinum. $Pt[P(m\text{-}C_6H_4CH_3)_3]_4$ was synthesized by hydrazine reduction in DMSO using a 4:1 mole ratio of ligand to metal. The pure product was isolated as yellow crystals from benzene-methanol (83%), mp 139–141°.

Anal. Calcd for $Pt[P(C_7H_7)_3]_4$: C, 71.42; H, 5.99; P, 8.77; Pt, 13.81. Found: C, 71.18, 71.49; H, 5.94, 4.9; P, 9.15; Pt, 13.68.

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[20] A. Seidel, "Solubilities of Organic Compounds," Vol. II, 3rd ed, Van Nostrand, Princeton, N. J., p 96.

[21] J. S. Fok, J. W. Robson, and F. C. Youngken, *Anal. Chem.*, **43**, 38 (1971).

[22] Both spectra showed the presence of some C_6H_6 which had not been removed by 0.5 hr of pumping on the solid.

[23] D. R. Coulson, *Inorg. Syn.*, **13**, 121 (1972).

[24] The much lower literature decomposition temperature of 110° [2a] was presumably determined in air.

Tris(triphenylphosphine)nickel.[25] $Ni[PPh_3]_3$ as a toluene solvate was prepared by refluxing 2.6 g of anhydrous nickel chloride and 21 g of triphenylphosphine in 300 ml of acetonitrile for 1 hr. After cooling to room temperature, 2.0 g of zinc dust was added. The mixture was stirred at room temperature under nitrogen overnight. The red solids remaining after filtration were dissolved in a minimal volume of hot toluene (60°). Filtration of the hot solution and precipitation with hexane gave a reddish brown powder, which was dried for an hour under vacuum: 16 g (70%), mp 124–126°.

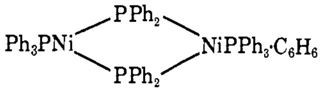
Anal. Calcd for $Ni[PPh_3]_3$: C, 76.7; H, 5.32; Ni, 6.9; P, 11.0. Calcd for $Ni[PPh_3]_3 \cdot 0.5C_7H_6$: C, 77.4; H, 5.50; Ni, 6.6; P, 10.4. Found: C, 76.7; H, 5.58; Ni, 6.5; P, 10.4.

The complexes $Pt[PPh_3]_3$,[26] $(C_2H_4)Pt[PPh_3]_2$,[5b] and $(C_2H_4)Ni[PPh_3]_2$[27] were prepared by literature procedures; $Pd[PPh_3]_4$ was kindly provided by Dr. J. J. Mrowca.

The arylphosphine ligands were obtained commercially and recrystallized from ethanol.[28]

Results

The preparations of a number of new arylphosphine platinum and palladium complexes are described in the Experimental Section. *p*- and *m*-tolylphosphines were used as ligands to enhance the solubility of the complexes and make them more amenable to physical studies, especially nmr. A synthesis is also given for $Ni[PPh_3]_3$, which appears in the literature[25] only as an item in a table of molecular weights but with a complete absence of details. This compound was the most difficult to characterize. It is extremely sensitive to O_2, tends to trap solvent when precipitated from solution, and decomposes in solution over several hours, even under rigorously O_2-free conditions. On standing, the deep-red solutions darken and a black precipitate[29] forms, which we have not characterized.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The tris(triphenylphosphine)nickel prepared by us has an elemental analysis corresponding quite closely to $Ni[PPh_3]_3 \cdot 0.5C_7H_8$. The residual toluene remained after 1 hour of pumping under vacuum at ambient temperature.

The nickel–ethylene complex is also thermally unstable but may be isolated in analytically pure form. The bright yellow benzene solutions slowly darken under N_2 or on exposure to vacuum. The darkening does *not* involve reversible dissociation of ethylene, since the original color cannot be restored by adding ethylene. Despite the instability of the complex, the nickel–ethylene bond is remarkably strong, since the starting complex is substantially recovered after its solution is pumped dry *in vacuo*. Decomposition may involve oxidative addition of an *o*-C–H group to nickel rather than ethylene dissociation as a first step.

The platinum–ethylene complex $(C_2H_4)Pt(PPh_3)_2$ was more thermally stable and could also be recovered from solution after pumping. When heated to about 80°, however,, the solution became reddish, possibly because Ugo's red cluster[10] is formed. The triarylphosphinepalladium and -platinum compounds were quite stable in the absence of O_2; solutions of $Pd[PPh_3]_4$ or $Pt[PPh_3]_3$ heated at 80° showed no signs of decomposition.

The molecular weights obtained on the compounds prepared in this work are shown in Table II, along with some literature values. Our values are very nearly half the theoretical for the ML_4 complexes and are close to the theoretical for ML_3 and $(C_2H_4)ML_2$ complexes. These results are consistent with extensive dissociation of the ML_4 complexes and no dissociation of the ML_3 or $(C_2H_4)ML_2$ complexes. Deviations of more than ±4% from 50 or 100% theoretical can be accounted for in terms of impurities known to be present in some of our samples.[30] The very low molecular weights found by Malatesta and coworkers for $Pd[PPh_3]_4$[2a] and $Pt[PPh_3]_3$,[2b] on the basis of which they proposed dissociation to ML_2 complexes (eq 3), presumably resulted from impurities in the samples and/or reactions of their samples with O_2.

Table II. Molecular Weights of Arylphosphine Complexes[a]

Complex	Calcd	Found	% theory	Lit. value
$Pt[PPh_3)_3$	981	833	85[e]	450[b]
$Pt[P(p\text{-}C_6H_4CH_3)_3]_3$	1108	1078	97	
$Pt[P(m\text{-}C_6H_4CH_3)_3]_3$	1108	1149	104	
$Pt[P(m\text{-}C_6H_4CH_3)_3]_4$	1412	655	46	
$Pd[PPh_3]_4$	1154	571	49	355[c]
$Pd[P(p\text{-}C_6H_4CH_3)_3]_3$	1019	1002	98	
$Pd[P(m\text{-}C_6H_4CH_3)_3]_3$	1019	1050	103	
$Ni[PPh_3]_3 \cdot 0.5C_7H_6$	595[f]	605	102[e,f]	790[d]
$(C_2H_4)Pt[PPh_3]_2$	747	668	89[e]	
$(C_2H_4)Ni[PPh_3]_2$	611	600	98	

[a] Cryoscopic in benzene as described in ref 21. [b] Reference 2b. [c] Reference 2a. [d] Reference 25, for unsolvated $Ni[PPh_3]_3$. [e] Proton nmr showed a small percentage of toluene impurity. [f] Assuming complete dissociation of toluene from $Ni[PPh_3]_3 \cdot 0.5C_7H_6$ (molecular weight 891).

Proton Nmr Spectra. Proton nmr spectral data for the ligands and their complexes are given in Table III. The effect of coordination on the arylphosphine resonances is generally to shift ortho protons to lower field while meta and para protons are shifted to higher field. The *p*-CH_3 group of $P(p\text{-}C_6H_4CH_3)_3$ shows little shift on coordination, while the *m*-CH_3 of $P(m\text{-}C_6H_4CH_3)_3$ shifts upfield by 0.17 ppm. The resonances of the complexed ethylene are shifted upfield ~2.7 ppm from their position for free ethylene at τ 4.75.

Phosphine ligand and ethylene were added to each of the solutions. Addition of L to a solution of ML_3 gave a spectrum showing only a single type of ligand, the chemical shifts of whose protons were intermediate between those of ML_3 and L.[31] This is the behavior expected for exchange which is rapid on the nmr time scale.

The multiplet patterns of the ligand ortho hydrogens behaved unusually. The ortho hydrogens of free P(*p*-

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(25) P. Heimbach, *Angew. Chem., Int. Ed. Engl.*, 3, 648 (1964).

(26) R. Ugo, F. Cariati, and G. La Monica, *Inorg. Syn.*, 11, 105 (1968).

(27) J. Ashley-Smith, M. Green, and F. G. A. Stone, *J. Chem. Soc. A*, 3019 (1968).

(28) Purification was necessary for PPh_3 and $P(p\text{-}C_7H_7)_3$. Otherwise addition of these ligands to solutions of the ML_3 complexes in the spectrophotometric experiments gave spectral changes which could be erroneously assigned to ML_4 formation at 25°.

(29) G. Herrmann, Ph.D. Thesis, Aachen, 1963, proposed structure 2 on the basis of analysis and degradation studies. Note the similarity with the Pt complex 1.

(30) A 1% toluene impurity in an otherwise pure compound of molecular weight 1000 would give an apparent molecular weight of 900, 10% low.

(31) Thus the $-CH_3$ resonance of $Pt[P(m\text{-}C_6H_4CH_3]_4$ appeared at τ 8.12, halfway between 8.03 and 8.20.

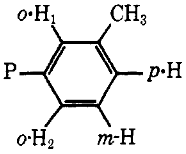
Table III. Proton Nmr Spectra[a] of Arylphosphines and Their Complexes in C_6D_6

Compound	o-H[b]	m- and p-H[b]	C_2H_4
PPh_3	2.59	2.92	
$Pt[PPh_3]_3$[c]	2.48	3.06	
$(C_2H_4)Pt[PPh_3]_2$[c]	2.46	3.02	7.41 (t, J_{Pt-H} = 60.0)[d,e]
$Pd[PPh_3]_4$	2.55	3.04	
$Ni[PPh_3]_3$[c]	2.63	3.04	
$(C_2H_4)Ni[PPh_3]_2$	2.50	3.03	7.43[e]

	o-H	m-H	$-CH_3$
P(p-$C_6H_4CH_3)_3$	2.58 (t, 8)	3.03 (d, 8)	7.97
Pt[P(p-$C_6H_4CH_3)_3]_3$	2.42 (d, 8)	3.20 (d, 8)	7.99
Pd[P(p-$C_6H_4CH_3)_3]_3$	2.43 (br)	3.19 (d, 8)	7.99

	o-H_1[f]	o-H_2[f]	m-H	p-H	$-CH_3$
P(m-$C_6H_4CH_3)_3$	2.59 (d, 9)	2.67 (t, 8)	2.91 (t, 8)	3.07 (d, 8)	8.03
Pt[P(m-$C_6H_4CH_3)_3]_3$	2.36	2.64 (d, 6)	3.07 (t, 8)	3.16 (d, 8)	8.20
Pd[P(m-$C_6H_4CH_3)_3]_3$	2.36	2.64 (d, 7)	3.04 (t, 8)	3.14 (d, 8)	8.20

[a] Chemical shifts are in τ units relative to TMS at 10.0. Coupling constants in parentheses are in hertz. Abbreviations used are: t, triplet; d, doublet; br, broad. [b] Unresolved multiplets. [c] These samples showed resonances due to a small amount of toluene impurity. [d] Also reported in ref 14. [e] Integrated areas of aromatic and olefinic protons correspond to the composition $(C_2H_4)M[PPh_3]_2$. [f] The proton designations for P(m-$C_6H_4CH_3)_3$ are as shown below.



$C_6H_4CH_3)_3$ appear as a triplet, assigned to coupling of ~8 Hz with both P and meta hydrogens. The ortho hydrogens of Pt[P(p-$C_6H_4CH_3)_3]_3$ appear only as a doublet, the coupling to P not being observed. With addition of 1 equiv of P(p-$C_6H_4CH_3)_3$ to the solution, the average ortho hydrogen resonance appears as a triplet with a coupling to P of 8 Hz. Similar behavior was found with the P(m-$C_6H_4CH_3)_3$ complexes of Pt and Pd, except that in these cases the two types of ortho hydrogens H_1 and H_2 (defined in Table II) changed from a singlet and a doublet to a doublet and a triplet, respectively, when equivalent amounts of P(m-$C_6H_4CH_3)_3$ were added to solutions of the ML_3 complexes. This behavior presumably involves relaxation of P–H coupling by a process involving P–P coupling.[32]

The effect on the proton nmr spectra of adding ethylene depends on the metal and the number of phosphine ligands present. $(C_2H_4)Ni[PPh_3]_2$ exhibits a sharp singlet due to C_2H_4 which stays sharp and migrates downfield as C_2H_4 is added, indicating a very fast exchange between free and coordinated C_2H_4. Addition of PPh_3 to the solution causes only a slight downfield shift, indicating a very favorable equilibrium constant for ethylene in competition with phosphine. As expected, adding C_2H_4 to $Ni[PPh_3]_3$ on a 1:1 basis gives a resonance near that of $(C_2H_4)Ni[PPh_3]_2$ (τ 7.43).

The palladium complexes behaved quite differently. Adding C_2H_4 to $Pd[PPh_3]_4$ gave a sharp resonance at τ 4.75, the position of free C_2H_4, indicating little or no olefin bonding. Adding C_2H_4 to the $Pd[P(C_7H_7)_3]_3$ complexes gave a sharp resonance at τ ~5.0, which moved back to 4.75 on adding an equivalent of phosphine. These results indicate a rapid ethylene exchange[33] but a very low olefin complex formation constant.

The platinum complexes showed the most unusual behavior. The spectrum of $(C_2H_4)Pt[PPh_3]_2$ shows a 1:4:1 triplet at τ 7.43 due to C_2H_4, with a 60-Hz coupling to ^{195}Pt and some unresolved fine structure due to P–H coupling.[14] Addition of C_2H_4 to the solution of $(C_2H_4)Pt[PPh_3]_2$ causes a broad new resonance to appear in the position of free C_2H_4 with a half-width of ~10 Hz. In this case exchange occurs at an intermediate rate: too slow to give a single average resonance but fast enough to give a broad free C_2H_4 resonance.[34] This, together with the absence of a resonance in the position of free C_2H_4 in the spectrum of $(C_2H_4)Pt[PPh_3]_2$, indicates that it does not dissociate in solution.[35] Further additions cause the free C_2H_4 resonance to grow in intensity with essentially no change in width. Simultaneously, the triplet resonance of bound C_2H_4 becomes increasingly broad, its area relative to the aromatic protons remaining constant. This behavior requires an associative mechanism, such as that shown in eq 5, with a small equilibrium constant for forming the bis(olefin) intermediate.

$$^*C_2H_4 + (C_2H_4)PtL_2 \rightleftharpoons (^*C_2H_4)(C_2H_4)PtL_2 \rightleftharpoons C_2H_4 + (^*C_2H_4)PtL_2 \quad (5)$$

Addition of PPh_3 to the above solution gives a single average C_2H_4 resonance at a chemical shift

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[32] A related type of behavior has been described by J. P. Fackler, Jr., J. A. Fetchin, J. Mayhew, W. C. Seidel, T. S. Swift, and M. Weeks, *J. Amer. Chem. Soc.*, 91, 1941 (1969).

[33] Adding C_2H_4 also restored the ortho hydrogen–P coupling which had been absent in the spectra of the tris complexes.

[34] The half-width indicates a half-life for free C_2H_4 of about 0.1 sec at 28°.

[35] The same conclusion was reached independently in ref 14. From our nmr spectra of $(C_2H_4)Pt(PPh_3)_2$ before and after added C_2H_4, we estimate that dissociation of 0.12 *M* starting complex to give 0.004 *M* free C_2H_4 would have been detectable. An upper limit on K_4 by this nmr criterion is $K_4 < 3.3 \times 10^{-4}$ *M*.

intermediate between 4.75 and 7.43. This ligand-catalyzed exchange of free and complexed ethylene is consistent with a mechanism involving a $(C_2H_4)PtL_3$ intermediate, as shown below.

$$(C_2H_4)PtL_2 + L \rightleftharpoons (C_2H_4)PtL_3 \rightleftharpoons C_2H_4 + PtL_3 \quad (6)$$

Addition of C_2H_4 to solutions of $Pt[P(C_7H_7)_3]_3$ gave a single average resonance at ~5.3. Its width (~50 Hz) indicates a much slower exchange[36] than in the Ni and Pd systems, and its chemical shift suggests an olefin formation constant K_1 intermediate between those of the Ni and Pd complexes.

^{31}P Nmr Spectra. ^{31}P nmr spectra of the compounds were determined as a function of temperature. Complexes of the three metals behaved in distinctly different ways. No ^{31}P resonances were apparent in the spectrum of a toluene solution of $Ni[PPh_3]_3$ at ambient temperature. On cooling, a broad resonance was first observed at -21 ppm (85% H_3PO_4) at $-50°$, which sharpened and moved to -23 ppm on further cooling to $-75°$, where part of the complex crystallized out. The spectrum of a solution with excess PPh_3 added still showed no resonances at room temperature. On cooling to $-25°$, a broad resonance was observed at $+6$ ppm, at the position of free ligand. On further cooling, this peak sharpened but did not move. No peaks assignable to NiL_3 or NiL_4 were observed. There were copious red-brown solids in the tube when it was removed from the spectrometer. Apparently the lower solubility of $Ni[PPh_3]_4$ compared to $Ni[PPh_3]_3$ caused the nickel to precipitate from solution before the temperature was lowered enough to slow the rapid exchange.

At room temperature, the $Pd[P(C_7H_7)_3]_3$ complexes showed a single resonance at -23 ppm. Lowering the temperature to $-90°$ had no effect on the spectrum. Addition of phosphine ligand gave a single resonance intermediate in chemical shift between -23 and $+8$ ppm (the free-ligand position). The single resonance observed at $-90°$ indicates an extremely fast ligand exchange, which prevented us from obtaining information on the stoichiometry of the palladium complexes from the ^{31}P spectra. $Pd[PPh_3]_4$ was so insoluble in toluene at ambient temperature that no resonance was observed. On heating to $+90°$ the solid dissolved and a single resonance was observed at -15 ppm.[37] Addition of PPh_3 to the hot solution caused the resonance to move upfield, a further indication of rapid exchange.

At ambient temperature, resonances of the platinum complexes $Pt[P(C_7H_7)_3]_3$ were so broad that they were difficult to see. On cooling, the spectra sharpened to show a 1:4:1 triplet due to coupling of the phosphorus to ^{195}Pt ($J_{PtP} = 4340$ Hz). Addition of 0.5 equiv of L at $-90°$ gave a new triplet assignable to PtL_4 ($J_{PtP} = 3780$ Hz).[38] A typical spectrum is shown in Figure 1.

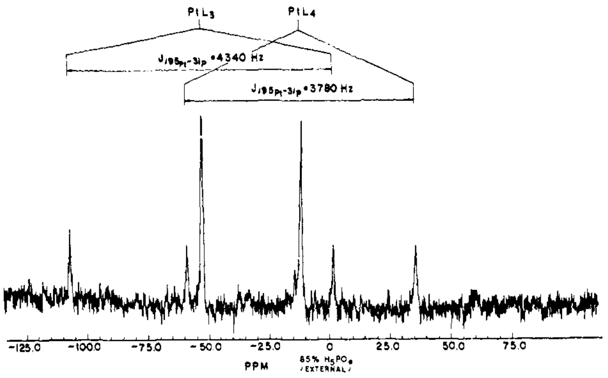

Figure 1. ^{31}P nmr spectrum (40.5 MHz) of 1 equiv of $Pt[P(p\text{-}C_6H_4CH_3)_3]_3$ and 0.5 equiv of $P(p\text{-}C_6H_4CH_3)_3$ in CH_2Cl_2–toluene at $-90°$.

The coupling constants are significantly less for PtL_4 than for PtL_3, as would be expected because of the reduced s character in the Pt–P bonds in the tetrakis complexes. If only the percentage of s character is considered, the ratio of coupling constants on going from sp^2 hybridization in PtL_3 to sp^3 in PtL_4 would be 0.75. This ratio has been observed in certain Ag(I)–phosphine systems,[39] but our value of 0.87 deviates significantly.

When resonances of PtL_3 disappeared, further ligand addition gave a new resonance in the position of free ligand. Thus, at $-90°$ the equilibrium constant for ligand association to PtL_4 is large and the exchange is slow. Addition of L to a solution of PtL_3 above $-80°$ destroyed the Pt–P coupling and gave only a single broad average resonance. A decrease in lifetime of ligand in the PtL_3 complex as a consequence of adding ligand to the solution is consistent with an *associative* exchange as indicated in eq 2.

$Pt[PPh_3]_3$ is so insoluble at low temperatures that spectral parameters were obtained on the supersaturated solution. Addition of PPh_3 caused $Pt[PPh_3]_4$ to precipitate.

$(C_2H_4)Pt[PPh_3]_2$ showed a 1:4:1 triplet ^{31}P resonance at room temperature which sharpened somewhat but did not shift appreciably on cooling. The ^{195}Pt–P coupling constant of 3660 Hz suggests a hybridization of Pt closer to sp^3 than to sp^2. The corresponding $(C_2H_4)Ni[PPh_3]_2$ behaved similarly on cooling but showed no resolved spin-spin coupling. The ^{31}P spectral data are collected in Table IV.

Table IV. ^{31}P Nmr Spectra of Arylphosphines[a] and Their Complexes in Toluene at $-90°$

Compound	Chemical shift, ppm	$J_{^{195}Pt-P}$, Hz
PPh_3	$+6$	
$Pt[PPh_3]_3$	-55^b	4370
$(C_2H_4)Pt[PPh_3]_2$	$-32^{d,e}$	3660
$Pd[PPh_3]_4$	-15^c	
$Ni[PPh_3]_3$	-23^d	
$(C_2H_4)Ni[PPh_3]_2$	-31^d	
$P(C_7H_7)_3{}^a$	$+8^e$	
$Pt[P(C_7H_7)_3]_3$	-51^e	4340
$Pt[P(C_7H_7)_3]_4$	-11^e	3780
$Pd[P(C_7H_7)_3]_3$	-23^e	

[a] Spectral data were the same for $P(p\text{-}C_6H_4CH_3)_3$ and $P(m\text{-}C_6H_4\text{-}CH_3)_3$. [b] At $-50°$. [c] At $+90°$. [d] At $-75°$. [e] In 50% toluene–50% CH_2Cl_2.

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(36) The addition of C_2H_4 to the PtL_3 solutions did not restore the ortho hydrogen–P coupling.

(37) This is the chemical shift expected for rapid exchange and complete dissociation of $Pd[PPh_3]_4$ into PPh_3 (+6 ppm) and $Pd[PPh_3]_3$ (−22 ppm).

(38) The chemical shift and coupling constant are identical with those observed at −90° in a solution of the isolated $Pt[P(m\text{-}C_6H_4CH_3)_3]_4$ complex.

(39) E. L. Muetterties and C. W. Alegranti, *J. Amer. Chem. Soc.*, **92**, 4114 (1970).

Table V. Electronic Spectral Data in Benzene at 25°

Complex	$\lambda_{\min}$[a] (ϵ)[b]	$\lambda_{\max}$ (ϵ)	$\lambda_{\max}$ (ϵ)	λ_{sh}[f] (ϵ)
PtL_3[c]	272 (1.4)	298 (2.9)	332 (3.0)	360 (1.5)
$Pt[P(m\text{-}C_6H_4CH_3)_3]_4$	282 (2.3)	297 (3.1)	332 (3.1)	360 (1.6)
PdL_3[d]	e	276 (2.7)	322 (3.0)	
$Pd[PPh_3]_4$	e	276 (3.4)	322 (3.0)	
$Ni[PPh_3]_3$	307 (0.6)		393 (1.4) broad	530 (0.25)
$(C_2H_4)Ni[PPh_3]_2$	e		303 (1.1) broad	380 (0.65)

[a] Wavelength in mμ. [b] Extinction coefficient in 10^4 cm^{-1} M^{-1}. [c] L = $P(p\text{-}C_6H_4CH_3)_3$, $P(m\text{-}C_6H_4CH_3)_3$, or PPh_3. [d] L = $P(p\text{-}C_6H_4CH_3)_3$ or $P(m\text{-}C_6H_4CH_3)_3$. [e] The short-wavelength minimum was below 270 mμ. [f] Slight, sloping shoulders were observed.

Electronic Spectra. The nature of the species present in benzene solution at 25° was confirmed and equilibrium constants for olefin complex formation were determined spectrophotometrically. Wavelengths and extinction coefficients of significant spectral features of isolated complexes are given in Table V. The PtL_3 complexes show three electronic transitions in the 270–700-mμ region, giving absorption maxima at 298 and 332 mμ and a slight shoulder at 360 mμ (Figure 2). Within the accuracy of the measurements, the wavelengths and extinction coefficients for the PtL_3 complexes are independent of L. The PdL_3 spectra are similar in appearance to those of PtL_3 except shifted 10–20 mμ to shorter wavelengths and with a less apparent shoulder at long wavelength. The $Ni[PPh_3]_3$ spectrum is quite different, exhibiting a single broad maximum at 393 and a slight shoulder at 530 mμ (Figure 3). The longer wavelength absorbance of the nickel complex makes its solutions deep red, whereas solutions of the triarylphosphine palladium and platinum complexes are yellow.

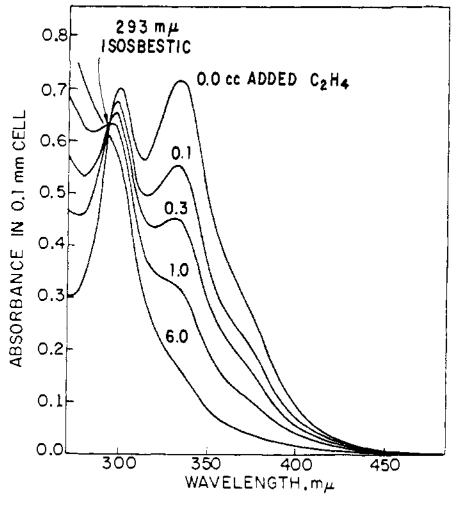

Figure 2. Electronic spectra of 2.39×10^{-3} M $Pt[PPh_3]_3$ with increasing volumes of added C_2H_4 gas in benzene at 25°.

Solutions of the ML_4 complexes gave spectra very similar to those of the corresponding ML_3 complexes except for increased absorbance in the 270–320 mμ region. This increased absorbance was just that expected from the presence of one equivalent of free L in a solution of ML_3, consistent with complete dissociation of the ML_4 complexes in solution. In fact, addition of 0.5 M $P(C_7H_7)_3$ or 1.0 M PPh_3 (which was more soluble) to solution of the ML_3 or ML_4 complexes had no effect on the spectra from 350 to 700 mμ, the region where L itself did not absorb at these concentrations. Thus we were unable to detect any association to form ML_4 complexes at 25° even with a very large excess of added ligand. A lower limit can be set on the ML_4 dissociation constant, $K_2 > 10$ M at 25°, for all these complexes.[40]

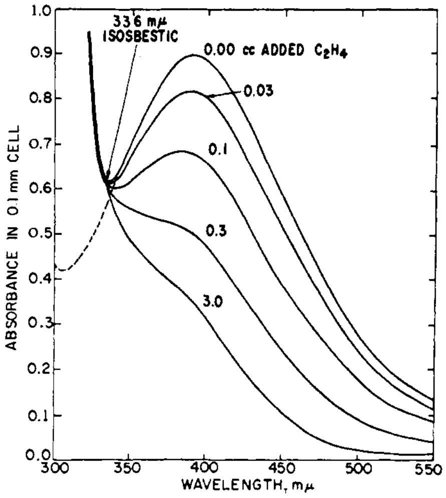

Figure 3. Electronic spectrum of 6.6×10^{-3} M $Ni[PPh_3]_3$ (— — —) and spectra of 6.6×10^{-3} M $Ni[PPh_3]_3$ + 0.5 M added PPh_3 with increasing volumes of added C_2H_4 gas (———) in benzene at 25°.

To determine whether the ML_3 complexes dissociate further, Beer's law was checked over a 100-fold variation in concentration of the complexes, by running spectra of 10^{-2}, 10^{-3}, and 10^{-4} M solutions in cells of 0.1-, 1.0-, and 10-mm path length. Except for $Ni[PPh_3]_3$, all the solutions obeyed Beer's law,[41] indicating that the ML_3 complexes did not dissociate further to a detectable extent. On this basis, an upper limit can be set on the ML_3 dissociation constant $K_3 < 10^{-6}$ M at 25°.[42]

In the case of $Ni[PPh_3]_3$, the deviation from Beer's law was attributable to slow irreversible decomposition rather than to reversible ligand dissociation. Addition of PPh_3 to the 10^{-4} M solution of the complex did not restore the spectrum of $Ni[PPh_3]_3$. The spectrum of $Ni[PPh_3]_3$ can also be determined starting from the $(C_2H_4)Ni[PPh_3]_2$ complex, which can be more easily obtained pure. Addition of excess PPh_3 to a freshly prepared yellow solution of $(C_2H_4)Ni[PPh_3]_2$ and purging with N_2 cause the solution to become deep

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(40) Assuming that formation of 5% ML_4 would have been detected spectrophotometrically in 0.5 M L solution.

(41) This means that the spectra were identical to within ±5%.

(42) Assuming that a 10% dissociation of ML_3 would have been detected in a 10^{-4} M solution.

red. The electronic spectrum shows the characteristic broad absorption maximum at 393 mμ. Comparison of this extinction coefficient with that obtained from our isolated sample of $Ni[PPh_3]_3$ showed the latter to be ~90% pure.

Equilibrium constants for ethylene complex formation *via* reaction 1 were determined by additions of C_2H_4 gas to a solution of ML_3 (or ML_4) complex as described in the Experimental Section. Spectra after such additions to $Pt[PPh_3]_3$ are shown in Figure 2. The isosbestic point at 293 mμ confirms the presence of two chromophoric species, namely $Pt[PPh_3]_3$ and $(C_2H_4)Pt[PPh_3]_2$. The slight deviation of the spectrum with 6.0 cm^3 of added C_2H_4 could represent the formation of a small concentration of $(C_2H_4)_2Pt[PPh_3]_2$.

Addition of C_2H_4 to a deep red solution of $Ni[PPh_3]_3$ turned the solution bright yellow. These color changes were accompanied by an isosbestic point at 336 mμ. The equilibrium constant for C_2H_4 complex formation was so large that it could not be readily determined unless PPh_3 was added to the solution. Spectra obtained after additions of ethylene to a solution of $Ni[PPh_3]_3$ containing 0.5 *M* PPh_3 are shown in Figure 3. The fact that the isosbestic point is also at 336 mμ in this solution confirms that the reaction involves only the chromophores $Ni[PPh_3]_3$ and $(C_2H_4)Ni[PPh_3]_2$.[43]

Values of K_1 for a variety of triarylphosphine complexes are listed in Table VI. Wavelengths of the isosbestic points for a given metal are independent of the ligand to within experimental error. Deviations from the isosbestic at high ethylene concentration were marked for the palladium complexes, suggesting higher concentrations of $(C_2H_4)_2ML_2$ for Pd than for Pt and Ni.

Table VI. Equilibrium Constants for Reaction in Benzene at 25°

$$ML_3 + C_2H_4 \overset{K_1}{\rightleftharpoons} (C_2H_4)ML_2 + L$$

ML_3	K_1	$\lambda_{\text{isobestic}}$
$Ni[PPh_3]_3$	$300^a \pm 40$	336^d
$Pt[P(p\text{-}C_6H_4CH_3)_3]_3$	0.21 ± 0.002	293
$Pt[PPh_3]_3$	0.122 ± 0.003	293
$Pt[P(m\text{-}C_6H_4CH_3)_3]_3$	$0.07^b \pm 0.02$	293^d
$Pd[P(p\text{-}C_6H_4CH_3)_3]_3$	0.016 ± 0.002	302
$Pd[PPh_3]_3$	$0.013^c \pm 0.002$	301
$Pd[P(m\text{-}C_6H_4CH_3)_3]_3$	0.004 ± 0.001	303

[a] Determined in the presence of 0.5 *M* added PPh_3. [b] Determined using $Pt[P(m\text{-}C_6H_4CH_3)_3]_3$. A value of 0.09 ± 0.03 was determined using $Pt[P(m\text{-}C_6H_4CH_3)_3]_4$. [c] Determined using $Pd[PPh_3]_4$. [d] The wavelength of the isobestic point did not change when L was added.

Equilibrium constants for olefin complex formation were also determined from proton nmr spectra of solutions of the ML_3 or ML_4 complexes to which C_2H_4 and, in some cases, L had been added. For these calculations the chemical shift of the average ethylene resonance was used to determine the fractions complexed and free.[44] Equilibrium constants determined by the nmr method gave the same rank order as in Table VI and agreed in all cases[45] within a factor of two with the more accurately determined spectrophotometric values, providing strong evidence for the nature of the reactions involved.

Discussion

Our results indicate that the ML_4 complexes studied are substantially dissociated in solution at ambient temperature into ML_3 and L.[46] Under these conditions free and complexed L exchange extremely rapidly, presumably by an associative mechanism involving ML_4 intermediates. Definitive evidence of PtL_4 complexes in solution was obtained from ^{31}P nmr studies at −90°.[47]

In view of the small equilibrium constants for formation of ML_4 complexes at ambient temperature, it is rather surprising that any of them can be obtained by crystallization. Crystal packing forces would appear to be involved. It may be that the metal atoms in some of the ML_4 compositions are not four-coordinate in the solid state. Thus the formula might be best represented as $ML_3 \cdot L$, with one phosphine simply trapped in the lattice. This formulation seems likely for $Ni[PPh_3]_4$, which has a red-brown color similar to that of $Ni[PPh_3]_3$. In the system with L = P(O-*o*-tolyl)$_3$, where we have been able to establish the existence of both NiL_4 and NiL_3 in benzene or toluene solution, the tris complex is red-orange while the tetrakis complex is colorless.[48]

Our results indicate that neither the ML_3 complexes nor the $(C_2H_4)ML_2$ complexes dissociate in solution. This conclusion disagrees with kinetic studies which gave dissociation constants of 1.6×10^{-4} and 3.0×10^{-3} *M* for $Pt[PPh_3]_3$ and $(C_2H_4)Pt[PPh_3]_2$.[6,7] Our results indicate that the dissociation constants must be smaller than the above values by at least an order of magnitude. The great stability of $(C_2H_4)Pt[PPh_3]_2$ to dissociation is indicated by its recovery after long-term exposure of its solution to vacuum.[35] The proton nmr line shape effects observed on adding C_2H_4 or PPh_3 to a solution of $(C_2H_4)Pt[PPh_3]_2$ are consistent with exchange by associative processes involving $(C_2H_4)_2PtL_2$ and $(C_2H_4)PtL_3$.

The results of our studies on the nature of the species in these solutions can be summarized by saying that all the species for which we have spectroscopic or kinetic evidence are complexes with 16 or 18 metal valence electrons. This behavior appears to be general for organometallic compounds of groups IVb through VIII.[49]

This work appears to be the first reported which permits comparison of formation constants for olefin complexes of the same type for three metals in a triad. The data in Table VI show that, for L = PPh_3, the equilibrium constant K_1 varies in the order Ni ≫ Pt > Pd. For a given metal with different ligands, K_1 varies in the order $P(p\text{-}C_6H_4CH_3)_3 > PPh_3 > P(m\text{-}C_6H_4CH_3)_3$. Subtle electronic and steric effects may operate in the

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(43) The added 0.5 *M* PPh_3 also absorbs at 336 mμ, but this contribution to the total absorbance stays effectively constant as C_2H_4 is added.

(44) Application of this technique to determine stability constants of olefin complexes of rhodium was described by R. Cramer, *J. Amer. Chem. Soc.*, **89**, 4621 (1967).

(45) Addition of C_2H_4 to a 0.1 *M* solution of $Pd[PPh_3]_4$ in C_6D_6 gave a resonance at the position of free C_2H_4, so that K_1 could not be determined by nmr in this case. The small fraction of $(C_2H_4)Pd[PPh_3]_2$ formed is a consequence of the mass action effect of the 0.1 *M* free PPh_3 which is present in the solution.

(46) This conclusion was arrived at earlier by Birk, *et al.*,[7] for $Pt[PPh_3]_4$.

(47) Greater formation of ML_4 complexes at low temperatures is expected if the ΔH for ligand dissociation is positive. See, for example, ref 48.

(48) L. W. Gosser and C. A. Tolman, *Inorg. Chem.*, **9**, 2350 (1970).

(49) C. A. Tolman, *Chem. Soc. Rev.*, in press.

case of tri-*m*-tolylphosphine. Comparison of tri-*p*-tolylphosphine with triphenylphosphine probably involves only an electronic effect; the larger value of K_1 with the more electron-donating phosphine[50] is consistent with a stronger metal–olefin bond because of greater π donation to the olefin from the metal.

Equation 1 involves both formation of a metal–olefin bond and breaking of a metal–phosphorus bond, so that the free energy change is a sum of terms. However, we suggest that changes in K_1 with changes in the metal reflect primarily changes in metal–olefin bond strength. If the strength of the metal–olefin bond depends primarily on π donation from the metal to the antibonding π^* ethylene orbitals, then the metal with the greatest electron availability should give the most stable ethylene complex. On the basis of ionization potentials of the gaseous d^{10} metal atoms, nickel (5.8 eV) should be a better π donor than Pd or Pt (each *ca.* 8.3 eV). The same conclusion can be reached on the basis of the promotion energies $(n-1)d^{10} \rightarrow (n-1)d^9np$ with Ni] (1.72 eV) being a much better donor than Pt (3.23 eV), which is better than Pd (4.23 eV).[18] Ease of electron promotion in the sequence Ni(0) $\gg$ Pt(0) $>$ Pd(0) is consistent with our electronic spectral data, where the longest wavelength maxima of the three M(PPh$_3$)$_3$ complexes are found at 393, 332, and 322 mμ, respectively. π-Donor ability of the zerovalent metals in this sequence may explain why Ni(0) forms a stable tetracarbonyl, whereas Pt(0) and Pd(0) do not, and is consistent with the results of X-ray crystal structure studies, which show a longer olefinic C–C bond length in (C$_2$H$_4$)Ni[PPh$_3$]$_2$ (1.46 Å) than in (C$_2$H$_4$)Pt[PPh$_3$]$_2$ (1.43 Å).[14]

Finally, a word should be said about why these triarylphosphine complexes dissociate to tris complexes, while tetrakis complexes of other ligands are very stable to dissociation. Meier, Basolo, and Pearson[51] have argued that Ni[P(OEt)$_3$]$_4$ does not dissociate appreciably in solution, while Ni[PPh$_3$]$_4$ does because triphenylphosphine is a better electron donor and builds up too much negative charge on the metal. Ligand-exchange studies on zerovalent nickel have since shown that the phosphorus bond strength is primarily a consequence of steric effects.[52] The large ligand cone angle[52] of 145° for PPh$_3$ makes coordination of four phosphines in a tetrahedral array extremely difficult. That dissociation is due to steric rather than electronic effects is nicely illustrated by the behavior of Ni[PMe$_3$]$_4$. Trimethylphosphine is a better donor than PPh$_3$, but is considerably smaller, with a ligand cone angle of 118°. Not only does Ni[PMe$_3$]$_4$ show no evidence of ligand dissociation in solution,[52] but the compound can be purified by sublimation *in vacuo* at 80°.[53] Further studies on equilibria involving the dissociation of other NiL$_4$ complexes will be described subsequently.[54]

Acknowledgments. We are indebted to Professor C. D. Cook for a copy of his paper[14] in advance of publication, and to Mrs. F. C. Youngken for molecular weight determinations.

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(50) C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 2953 (1970).

(51) M. Meier, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, **8**, 795 (1969).

(52) C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 2956 (1970).

(53) H. F. Klein and H. Schmidbauer, *Angew. Chem.*, **82**, 885 (1970).

(54) Note Added in Proof. A correlation between chemical properties and the frequency of the longest wavelength electronic transition has been noted by L. Vaska, L. S. Chen, and W. V. Miller, *J. Amer. Chem. Soc.*, **93**, 6671 (1971), for reactions of M[*cis*-(C$_6$H$_5$)$_2$PCHCHP(C$_6$H$_5$)$_2$]$^+$ complexes (M = Co, Rh, and Ir). The reactivity order found for oxidative addition reactions, Co > Ir > Rh, parallels our results on the ease of ethylene complex formation of the nickel triad.

Organometallic Conformational Equilibria. XV. Preparation and Resolution of 1,2,3-h^3-(1-Acetyl-2,3-dimethylallyl)-[(*S*)-α-phenethylamine]chloropalladium[1]

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Abstract: (+)-Bis[1,2,3-h^3-1-acetyl-2,3-dimethylallyl)chloropalladium(II)] and some of its amine derivatives are reported. These complexes will not epimerize, but they do isomerize.

The 1,2,3-h^3-(1-acetyl-2-methallyl)[(*S*)-α-phenethylamine]chloropalladium complex, which can be isolated in optically active form,[2–4] epimerizes rapidly in solution at ambient temperatures. It has been firmly established that the predominant mechanism whereby substituted π-allyl–palladium chloride complexes epimerize or racemize is *via* formation of a σ-bonded intermediate.[2–4] Our study of model allyl compounds showed that thermodynamic constraints are placed upon such rearrangements, suggesting the possibility of isolation of an allylic moiety which would not epimerize.[3] It was generalized that a chiral 1,2,3-trisubstituted allyl moiety with two different groups occupying the positions at the terminal

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