Since the present calculation differs a little from the previous, two of the complexes (Co(*p*-COOH)TPP in pyridine and CoTPyP in H_2TPyP) treated before are recalculated here for direct comparison. The set of orbital energies, V_1, V_2, and V_3 ($V_1 = E(\mathrm{b}_1) - E(\mathrm{a}_1)$, $V_2 = E(\mathrm{b}_1) - E(\mathrm{e})$, $V_3 = E(\mathrm{b}_1) - E(\mathrm{b}_2)$), which yield acceptable g values are found to be not entirely unique. However, the values vary within finite ranges, and three representative calculations for each system are shown here in order to cover the allowed variations. The experimental data are given in Table II and the calculated data in Table III.

As can be seen from Table III, for unsolvated complexes CoTPyP and CoOEP, the allowed variations in V_1 and V_2 are not large. The variation in V_3 is appreciable and indicates that the method is not sensitive enough to evaluate V_3 accurately. For the case of solvent coordinated complex, although the variations in V_1 and V_2 are quite appreciable when viewed separately, the difference, $V_2 - V_1$ (i.e., $E(\mathrm{a}_1) - E(\mathrm{e})$), however does not vary. This shows that $g_{\|}$ and $g_{\perp}$ are very sensitive to a change in (V_2–V_1). In all cases however, the values of P and κ are seen to be insensitive toward variations in V_i. The values of K (=$P\kappa$) calculated previously by the perturbation method for CoTPyP and the (2:1) solvent-coordinated complex were −0.0125 and 0.0043, respectively.[10] These compare fairly well with the present figures. The value of P for CoOEP is very nearly the free-ion value of 0.0254 while that for CoTPyP is slightly lower. The much lower value of $P = 0.018$ for the solvated complex is in agreement with the fact that the unpaired electron is delocalized through σ bonding from the Co d_{z^2} orbital to the nitrogen orbitals of the two solvent molecules.

In concluding this note, it must be mentioned that although in previous calculations[1] which neglected the configuration interaction, the values of V_3 were found to be much smaller, all the conclusions drawn in that study are still valid nevertheless. For instance, the excited state $^4B_2$ is still found to be coupled to the ground state $^2A_1$ to a large extent in unsolvated cobalt porphyrins.

Appendix

When the Kramer doublet, $|+\rangle, |-\rangle$, is expressed as

$$|+\rangle = \sum_{i=0}^{15} \eta_i |\psi_i\rangle \qquad |-\rangle = \sum_{i=0}^{15} \eta_i |\psi_i'\rangle$$

with $|\psi_i\rangle, |\psi_i'\rangle$ defined as before,[1] the matrix elements $\langle +|\sum_k a_{kz}|+\rangle$ and $\langle -|\sum_k a_k^-|+\rangle$ in eq 1 and 2 turn out to be as follows:

$$\langle +|\sum_k \mathrm{a}_{kz}|+\rangle = 2\eta_0^2 - \eta_1^2 + \eta_2^2 + 3\eta_3^2 + \eta_4^2 - 5\eta_5^2 - 6\eta_6^2 + 2(\eta_7^2 + \eta_8^2 - \eta_9^2 - \eta_{10}^2) - 3\eta_{12}^2 + 5\eta_{13}^2 - \eta_{14}^2 - \eta_{15}^2 - \sqrt{6}\eta_0\eta_1 - 3\sqrt{2}\eta_0(\eta_2 + \eta_3) - 3\sqrt{2}\eta_1(\eta_9 - \eta_{11}) - \sqrt{6}(\eta_2\eta_9 - \eta_3\eta_{11} + \eta_5\eta_{10} - \eta_6\eta_{12} + \eta_7\eta_{15} + \eta_8\eta_{14})$$

$$\langle -|\sum_k a_k^-|+\rangle = -2\eta_0^2 - 6\eta_1^2 + \sqrt{6}(\eta_0\eta_1 + \eta_2\eta_{11} - \eta_3\eta_9 - \eta_4\eta_9 - \eta_6\eta_{13} + \eta_7\eta_{14} + \eta_8\eta_{15}) - 3\sqrt{2}(\eta_0\eta_4 + \eta_0\eta_5 - \eta_1\eta_{10}) - 4\sqrt{3}\eta_1\eta_4 + 4(\eta_2\eta_3 - \eta_2\eta_5 + \eta_6\eta_7 + \eta_6\eta_8 - \eta_7\eta_8 + \eta_7\eta_{10} + \eta_{12}\eta_{14} + \eta_{12}\eta_{15}) + 2(\eta_2\eta_4 - \eta_{12}\eta_{13}) - 12(\eta_9\eta_{11} + \eta_{14}\eta_{15})$$

Registry No. Co(*p*-COOH)TPP(py)$_2$, 58512-42-8; CoTPyP, 14244-55-4; CoOEP, 17632-19-8.

Supplementary Material Available: Table I showing the energy matrix (1 page). Ordering information is given on any current masthead page.

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Aspects of the Low-Temperature Chemistry of Tris(triphenylphosphine)platinum(0)

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A distinctive feature of the chemistry of platinum(0) phosphine and related d^{10} complexes is the accessibility of a range of stable coordination numbers.[1,2] This is reflected in the occurrence of stable complexes with coordination numbers ranging from 2 to 4, e.g., [Pt(P(*i*-Pr)$_3$)$_2$],[3] [Pt(PPh$_3$)$_3$],[4] and [Pt(PEt$_3$)$_4$][5] (the preferred coordination number being influenced by both steric and electronic factors)[6] and in the duality of mechanisms exhibited, for example, by [Pt(PPh$_3$)$_3$], which has been shown to undergo substitution and oxidative addition reactions simultaneously by associative and dissociative mechanisms.[7,8]

In some instances Pt(0) combines with a given ligand to form two or more stable complexes with different coordination numbers. Thus, [Pt(PPh$_3$)$_3$] and [Pt(PPh$_3$)$_4$] are both stable compounds in the solid state.[4] However, [Pt(PPh$_3$)$_4$] has been reported[9] to dissociate completely (to [Pt(PPh$_3$)$_3$] and PPh$_3$) in solvents such as benzene or toluene. (Although kinetic evidence supports a dissociative mechanism for certain substitution reactions of [Pt(PPh$_3$)$_3$],[7,10] [Pt(PPh$_3$)$_2$] does not appear to have been identified or characterized in solution.[11]) Virtually all reported studies pertaining to the association–dissociation and substitution reactions of [Pt(PPh$_3$)$_3$] in solution have been conducted at ambient temperatures. We now report the extension of such studies to lower temperatures (down to −100 °C) where we have found the solution chemistry of [Pt(PPh$_3$)$_3$] to be significantly different from that at room temperature. Of pertinent interest is one prior investigation involving the closely related [Pt(P(*p*-C$_6$H$_4$CH$_3$)$_3$)$_n$] system.[13]

Reaction with PPh$_3$. At room temperature only a very broad ^{31}P NMR signal was observed for a toluene solution of [Pt(PPh$_3$)$_3$]. When the solution was cooled to −70 °C, the resonances sharpened to give the characteristic line due to [Pt(PPh$_3$)$_3$] (δ 49.9) together with two ^{195}Pt satellites ($J_{\mathrm{Pt-P}}$ = 4438 Hz; see Table I). Addition of 0.5 equiv of PPh$_3$ to this solution resulted in broadening of the NMR signal. However, further cooling of the solution to −100 °C caused the spectrum to sharpen, revealing two signals assignable to [Pt(PPh$_3$)$_3$] and [Pt(PPh$_3$)$_4$], respectively (see Figure 1 and Table I). No signal due to free PPh$_3$ could be detected. Thus, it is concluded that

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(11) The isolation of solid "[Pt(PPh$_3$)$_2$]" and examination of some of the chemistry of this substance in solution have been claimed.[12] However, subsequent attempts to prepare [Pt(PPh$_3$)$_2$] *in monomeric form* under conditions where it is sufficiently stable for direct detection and characterization, either in solution or as a solid, appear to have been unsuccessful.

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0020-1669/80/1319-1073$01.00/0

Table I. ^{31}P NMR Parameters[a]

compd	δ	J_{Pt-P}, Hz
$[Pt(PPh_3)_3]$	49.9	4438
$[Pt(PPh_3)_4]$	9.2	3829
$[Pt(PPh_3)_2(O_2)]$	16.4	4059
$[Pt(PPh_3)_2(C_2H_4)]$	32.5	3694
$[Pt(PPh_3)_2(C_4H_6)]$	31.7	3756
	31.5	3778
$[Pt(PPh_3)_3(CO)]$	12.3	3537
$[Pt(PPh_3)_2(CO)_2]$	7.7	3232
PPh_3	−9.0	

[a] Measured in toluene solution at temperatures in the range −80 to −100 °C.

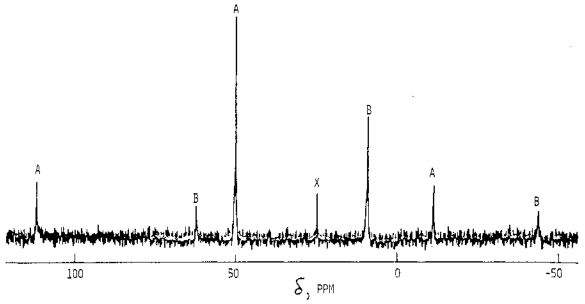


Figure 1. ^{31}P NMR spectrum of a toluene solution containing $[Pt(PPh_3)_3]$ and 0.5 equiv of PPh_3 at −100 °C: A, $[Pt(PPh_3)_3]$; B, $[Pt(PPh_3)_4]$; X, Ph_3PO (impurity).

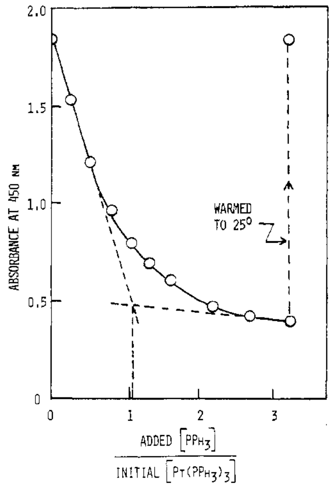


Figure 2. Spectral titration of a toluene solution containing 6.3 × 10^{-3} M $[Pt(PPh_3)_3]$ with PPh_3 at −80 °C (1-cm light path).

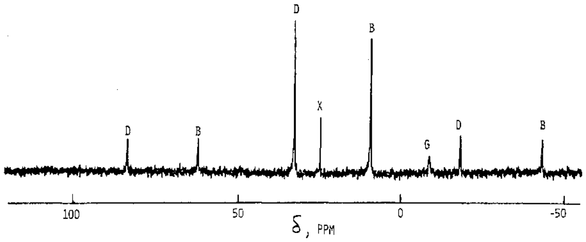


Figure 3. ^{31}P NMR spectrum of a toluene solution of $[Pt(PPh_3)_3]$, saturated with ethylene at −80 °C and then cooled to −100 °C: B, $[Pt(PPh_3)_4]$; D, $[Pt(PPh_3)_2(C_2H_4)]$; G, PPh_3; X, Ph_3PO (impurity).

at −100 °C the equilibrium corresponding to the formation of $[Pt(PPh_3)_4]$, according to eq 1, lies far to the right. A

$$[Pt(PPh_3)_3] + PPh_3 \rightleftarrows [Pt(PPh_3)_4] \qquad (1)$$

similar result has previously been reported for the $[Pt(P(p\text{-}C_6H_4CH_3)_3)_3]$–$[Pt(P(p\text{-}C_6H_4CH_3)_3)_4]$ system.[13]

The formation of $[Pt(PPh_3)]_4$ according to eq 1 also was confirmed spectrophotometrically at −80 °C. Incremental addition of PPh_3 to a toluene solution of $[Pt(PPh_3)_3]$ resulted in a spectral change attributable to the formation of a new species, $[Pt(PPh_3)_4]$ (isosbestic point at 430 nm, $\epsilon = 6.6 \times 10^2$ M^{-1} cm^{-1}). Spectral titration at 450 nm confirmed the 1:1 stoichiometry of the reaction between $[Pt(PPh_3)_3]$ and PPh_3, in accord with eq 1. From the spectral titration curve (Figure 2) the equilibrium constant of reaction 1 at −80 °C could be estimated to be ca. 3 × 10^4 M^{-1}. Warming the final titration solution, containing 6.3 × 10^{-4} M $[Pt(PPh_3)_4]$ and ca. 10^{-2} molar excess PPh_3, from −80 °C to room temperature resulted in restoration of the original spectrum of $[Pt(PPh_3)_3]$, confirming that dissociation of $[Pt(PPh_3)_4]$ under these conditions is complete. Thus, the equilibrium corresponding to reaction 1 is displaced almost completely from right to left on warming from −80 °C to room temperature.

Reactions with Monoolefins. On saturation of a toluene solution of $[Pt(PPh_3)_3]$ with ethylene at −80 °C, the ^{31}P NMR signals of $[Pt(PPh_3)_3]$ disappeared and only broad resonances due to $[Pt(PPh_3)_2(C_2H_4)]$ could be discerned. However, when the solution was cooled to −100 °C, the spectrum sharpened to reveal two signals (each with ^{195}Pt satellites) assignable to $[Pt(PPh_3)_4]$ and $[Pt(PPh_3)_2(C_2H_4)]$, respectively (Figure 3 and Table I). These observations are consistent with the quantitative occurrence of reaction 2.

$$2[Pt(PPh_3)_3] + C_2H_4 \rightarrow [Pt(PPh_3)_4] + [Pt(PPh_3)_2(C_2H_4)] \qquad (2)$$

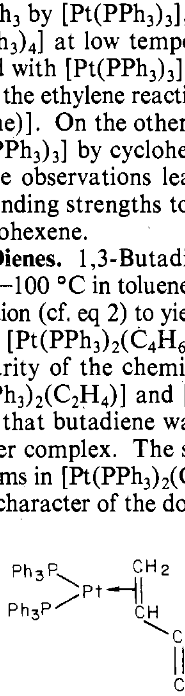
It is significant that the displacement of PPh_3 from $[Pt(PPh_3)_3]$ by C_2H_4 at 25 °C is unfavorable, the equilibrium constant for reaction 3 having been estimated to be 0.12.[13]

$$[Pt(PPh_3)_3] + C_2H_4 \rightleftarrows [Pt(PPh_3)_2(C_2H_4)] + PPh_3 \qquad (3)$$

The driving force for this displacement at lower temperature thus appears to be associated, at least in part, with the "scavenging" of the displaced PPh_3 by $[Pt(PPh_3)_3]$, i.e., with the enhanced stability of $[Pt(PPh_3)_4]$ at low temperatures.

1-Hexene reacted with $[Pt(PPh_3)_3]$ at low temperatures, in a manner similar to the ethylene reaction, to form the complex $[Pt(PPh_3)_2(\text{1-hexene})]$. On the other hand, no displacement of PPh_3 from $[Pt(PPh_3)_3]$ by cyclohexene could be detected at −100 °C. These observations lead to the following expected[14] order of binding strengths to $[Pt(PPh_3)_2]$: ethylene > 1-hexene > cyclohexene.

Reactions with Dienes. 1,3-Butadiene was found to react with $[Pt(PPh_3)_3]$ at −100 °C in toluene, in a manner analogous to the ethylene reaction (cf. eq 2) to yield an equimolar mixture of $[Pt(PPh_3)_4]$ and $[Pt(PPh_3)_2(C_4H_6)]$ characterized by ^{31}P NMR. The similarity of the chemical shifts and coupling constants of $[Pt(PPh_3)_2(C_2H_4)]$ and $[Pt(PPh_3)_2(C_4H_6)]$ (see Table I) suggested that butadiene was bound to Pt as a monoolefin in the latter complex. The slight inequivalence between the two P atoms in $[Pt(PPh_3)_2(C_4H_6)]$ is consistent with the unsymmetrical character of the double bond in a structure such as **1**.



1

The compound $[Pt(PPh_3)_2(C_4H_6)]$ was synthesized by an independent route (see Experimental Section) and found to exhibit a ^{31}P NMR spectrum in toluene solution identical with

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[14] Tolman, C. A. *J. Am. Chem. Soc.* **1974**, *96*, 2780.

that of the product of the in situ reaction of $[Pt(PPh_3)_3]$ and butadiene at low temperatures. The proposed "monodentate" structure (1) is supported by the infrared spectrum of $[Pt(PPh_3)_2(C_4H_6)]$ (Nujol mull), which contains a sharp band at 1605 cm^{-1}, consistent with the expected stretching frequency of an uncoordinated C=C bond. A similarly assigned band at 1608 cm^{-1} has previously been reported for the platinum(II) compound $[PtCl_2(C_4H_6)]_2$.[15]

By analogy with the case of cyclohexene, no displacement of PPh_3 from $[Pt(PPh_3)_3]$ by 1,5-cyclooctadiene could be detected at −100 °C.

Other Reactions. O_2 did not react with $[Pt(PPh_3)_3]$ in toluene solution below −70 °C. At −70 °C, a reaction analogous to that with C_2H_4 was observed (eq 4). At somewhat

$$2[Pt(PPh_3)_3] + O_2 \rightarrow [Pt(PPh_3)_4] + [Pt(PPh_3)_2(O_2)] \quad (4)$$

higher temperatures (ca. −45 °C), O_2 also reacted with $[Pt(PPh_3)_4]$ in toluene solution according to eq 5. The formation

$$[Pt(PPh_3)_4] + O_2 \rightarrow [Pt(PPh_3)_2(O_2)] + 2PPh_3 \quad (5)$$

of $[Pt(PPh_3)_2(O_2)]$ by O_2 displacement of PPh_3 from $[Pt(PPh_3)_3]$ has previously been postulated as a step in the $[Pt(PPh_3)_3]$-catalyzed oxidation of PPh_3 by O_2.[9,16]

Passing CO through a toluene solution of $[Pt(PPh_3)_3]$ at −80 °C resulted in the formation of $[Pt(PPh_3)_3(CO)]$[4] according to eq 6. Warming to −65 °C resulted in further

$$[Pt(PPh_3)_3] + CO \rightarrow [Pt(PPh_3)_3(CO)] \quad (6)$$

reaction to form $[Pt(PPh_3)_2(CO)_2]$[4] with displacement of PPh_3 (eq 7). The higher temperature required for the latter reaction

$$[Pt(PPh_3)_3(CO)] + CO \rightarrow [Pt(PPh_3)_2(CO)_2] + PPh_3 \quad (7)$$

presumably reflects the fact that $[Pt(PPh_3)_3(CO)]$ is an 18-electron complex and therefore undergoes substitution by a dissociative mechanism.

Experimental Section

$[Pt(PPh_3)_3]$,[17] $[Pt(PPh_3)_4]$,[17] $[Pt(PPh_3)_2(C_2H_4)]$,[18] $[Pt(PPh_3)_3(CO)]$,[19] and $[Pt(PPh_3)_2(O_2)]$[20] were prepared by the literature procedures cited.

$[Pt(PPh_3)_2(C_4H_6)]$. $[Pt(PPh_3)_2(O_2)]$ (0.3 g) was dissolved in ethanol (10 mL), and the resulting solution was saturated with 1,3-butadiene. A solution of $NaBH_4$ (0.02 g) in ethanol (5 mL) was then added dropwise with stirring, while butadiene was passed through the solution. After a few minutes a pale yellow solid precipitated. This was collected by filtration, washed with water and ethanol, and dried under vacuum: yield 0.18 g (59%); mp 126–128 °C (uncor). Anal. Calcd for $[Pt(PPh_3)_2(C_4H_6)]$: C, 62.1; H, 4.7; P, 8.0. Found: C, 62.0; H, 4.8; P, 8.0.

Spectral Measurements. UV–visible spectra were recorded with a Cary 14 spectrophotometer and infrared spectra with a Beckman IR10 spectrophotometer. ^{31}P NMR spectra were determined with a Bruker HX-90E spectrometer interfaced with a Nicolet 1080 computer. A spectrometer frequency of 36.434 MHz was used. The spectra were determined in the pulsed FT mode and were broad-band proton decoupled. Concentrations of the platinum complexes were typically in the range from 1×10^{-2} to 5×10^{-2} M. Chemical shifts (δ) are reported relative to 85% H_3PO_4 at room temperature.

Elemental analyses were performed by Galbraith Laboratories.

Because most of the compounds encompassed by these studies are sensitive to oxygen, all manipulations and experiments were performed under a nitrogen atmosphere, using solvents which had been deoxygenated by purging with nitrogen.

Acknowledgment. Support of this research through a grant from the National Science Foundation is gratefully acknowledged. We thank Engelhard Minerals and Chemicals Corp. for a generous loan of platinum. The NMR facilities used in this research were supported in part through the University of Chicago Cancer Center (Grant No. NIH-CA-14599).

Registry No. $Pt(PPh_3)_3$, 13517-35-6; $Pt(PPh_3)_4$, 14221-02-4; $Pt(PPh_3)_2(O_2)$, 15614-67-2; $Pt(PPh_3)_2(C_2H_4)$, 12120-15-9; $Pt(PPh_3)_2(C_4H_6)$, 72347-07-0; $Pt(PPh_3)_3(CO)$, 15376-99-5; $Pt(PPh_3)_2(CO)_2$, 15377-00-1; PPh_3, 603-35-0.

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Assignment of the Elusive Metal–Ligand T_{1u} Stretching Vibration in Hexaammineruthenium(II) Salts

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Infrared and Raman spectra of octahedral hexaammine complexes constitute one of the most thoroughly investigated areas of vibrational spectroscopy in the realm of inorganic coordination complexes.[1] In view of the role of the vibrational contribution to the activation energy required for electron transfer in self-exchange reactions for species such as $M(NH_3)_6^{(n,n+1)}$[2] the absence of complete infrared data which has persisted in the literature for the hexaammineruthenium(II) cation is somewhat puzzling. A survey of infrared data listed by Nakamoto for fifteen octahedral hexaammine complexes with chloride as the counterion reveals that only for $[Ru(NH_3)_6]Cl_2$ is the infrared ν(M–N) frequency absent.[1] Recent infrared studies of $[Ru(py)_6](BF_4)_2$ in our laboratory revealed an extremely weak absorption in the low-frequency infrared region which was attributed to the infrared allowed T_{1u}(Ru–N) stretching mode.[3] The $Ru(py)_6^{2+}$ metal–ligand vibration was analyzed by treating the pyridine ligands as rigid groups in order to employ an MX_6 model for comparing the ratio of the ruthenium–nitrogen force constants in $Ru(py)_6^{2+}$ and $Ru(NH_3)_6^{3+}$. A desire to include the $Ru(NH_3)_6^{2+}$ cation in these studies led us to undertake the infrared characterization of a series of hexaammineruthenium(II) salts in order to unambiguously identify the elusive metal–ligand stretching frequency in these complexes. The results of our infrared studies are reported herein.

Experimental Section

Hexaammineruthenium(II) salts were prepared according to the procedure of Schreiner and Lin.[4] Following the zinc reduction step the aqueous solution containing $[Ru(NH_3)_6]^{2+}$ was carefully filtered under a nitrogen atmosphere into a saturated solution of the appropriate NH_4X salt, and the resultant two layers were allowed to diffuse together over a period of days to promote slow formation of crystalline $[Ru(NH_3)_6]X_2$. Purity of the samples was confirmed by potentiometric titration with standardized silver nitrate solution for the halide salts. The infrared spectra provided additional confirmation of sample purity since the most probable contaminants each display at least one characteristic infrared absorption which is evident at low concentrations and does not overlap any $[Ru(NH_3)_6]^{2+}$ band: NH_4X, ~1400 cm^{-1};

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