H_2. Complex **8** reacted with CO to form the carbonyl adduct, $[Rh(PN)_2(CO)]^+$ (**9**), whereas the iridium analogue reacted with CO to form a complex mixture of products. The carbonyl adduct of **1**, $[Ir(PN)_2(CO)]^+$ (**5**), however, was synthesized from $Ir(PN)_2(CO)Cl$ (**3**) with KPF_6, which was synthesized from the reaction of $[Ir(CO)_2Cl_2]^-$ with 2 equiv of PN. The structure of **5** was determined to be four-coordinate with one monodentate PN ligand, which is surprising when compared to the five-coordinate structures of the diphosphine analogues $[Ir(dppe)_2(CO)]^+$, $[Ir(dppp)_2(CO)]^+$, and $[Ir(dppm)_2(CO)]^+$ and the rhodium analogue $[Rh(PN)_2(CO)]^+$ (**9**). The reactivity of **5** with H_2 and H^+ was also examined since compound **5** was found to be present in the benzaldehyde solutions of catalytic decarbonylation experiments using complex **1**.

Unfortunately, the PN complexes of rhodium were not good catalysts for the decarbonylation of benzaldehyde: $[Rh(PN)_2]BF_4$ showed an activity for the formation of benzene of 10 turnovers/h at 150 °C compared to 1.1×10^2 turnovers/h for $[Rh(dppp)_2]BF_4$. The opposite trend was observed for the iridium analogues; compound **1** was found to be a better catalyst for the decarbonylation of benzaldehyde than the iridium bis(diphosphine)catalysts. This trend is consistent with the mechanism proposed for the $[Rh(dppp)_2]^+$ catalyst system, and the increased rate results from the increased lability of the Ir–N bond relative to Ir–P. Also, the most probable reason for the slower decarbonylation rate for **8** relative to $[Rh(dppp)_2]^+$ is the slower rate for oxidative addition; however, slow Rh–N bond rupture can not be totally ruled out.

These conclusions should be treated with some caution, however, since they are based on the assumption that the mechanisms of these two catalyst systems are identical with that postulated for $[Rh(dppp)_2]^+$. Detailed kinetic studies have not been carried out for the iridium complexes. Seemingly slight changes in the electronic and steric properties of a complex can drastically affect the activity and mechanism of a catalyst. Furthermore, the observation of intermediates can be misleading when studying mechanisms of catalytic reactions. For example, in the case of **1**, it is possible that $[Ir(PN)_2(CO)]^+$ (**5**) is the active catalyst and undergoes oxidative addition of the aldehyde without prior loss of CO. This is a reasonable proposal since **5** will oxidatively add H_2 at 1 atm and 25 °C to form $[Ir(PN)_2(H)_2(CO)]^+$ (**6**). If this mechanism were operative for **1**, then the true rate-determining step might be Ir–N bond rupture or oxidative addition. Clearly, more kinetic and chemical studies are needed to understand the mechanism of these reactions.

Acknowledgment. This work was supported by the National Science Foundation. We gratefully acknowledge the Johnson Matthey Co. for a generous loan of Rh and Ir salts. A.L.C. also thanks the National Science Foundation for a Graduate Fellowship. M.P.A. acknowledges the U.S. Air Force Institute of Technology Graduate School Program, and B.M.M. acknowledges the Graduate School of Creighton University for a Summer Faculty Research Fellowship.

Registry No. **1**(PF_6), 113705-90-1; **2**(PF_6), 113705-92-3; **3**, 113705-93-4; **4**·Et_2O, 113705-95-6; **5**(PF_6), 113705-97-8; **6**(PF_6), 113705-99-0; **7**(BF_4)$_2$, 113706-01-7; **8**(PF_6), 113706-02-8; **8**(BF_4), 107810-34-4; **9**(PF_6), 113706-04-0; **10**, 113706-05-1; **11**, 113706-06-2; PN, 60398-55-2; $[Ir(PN)(cod)]PF_6$, 112021-45-1; H_2, 1333-74-0; $Li[Ir(CO)_2Cl_2]$, 55095-92-6; $[Rh(nbd)Cl]_2$, 12257-42-0; D_2, 7782-39-0; $[Ir(dppp)_2]PF_6$, 113706-08-4; $[Ir(cod)Cl]_2$, 12112-67-3; $[Rh(dppp)(PN)]^+$, 113706-09-5; benzaldehyde, 100-52-7.

Supplementary Material Available: Listings of general temperature factor expressions, final positional and thermal parameters for all atoms including solvate molecules, calculated hydrogen atom positions, distances and angles, and least-squares planes (25 pages); listings of observed and calculated structure factor amplitudes (52 pages). Ordering information is given on any current masthead page.

Notes

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^{195}Pt{^{1}H} and ^{31}P{^{1}H} NMR Investigation of the Platinum(0)–Tetraphosphine Complexes $Pt[CH_3C(CH_2PPh_2)_3]PR_3$

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Received April 21, 1987

Platinum(IV) and platinum(II) complexes have been investigated extensively by ^{195}Pt NMR spectroscopy, usually by use of INDOR techniques; in contrast, the amount of ^{195}Pt NMR data available on mononuclear platinum(0) complexes is limited.[1,2] Data concerning the magnitudes of Pt–P coupling constants and ^{195}Pt and ^{31}P chemical shifts for Pt(0)–phosphine complexes are particularly limited due to the tendency of $Pt(PR_3)_4$ compounds to dissociate in solution. By use of the chelating triphosphine ligand $CH_3C(CH_2PPh_2)_3$ ("tripod") a series of dissociatively stable $Pt(tripod)PR_3$ complexes (PR_3 = PMe_2Ph, $PMePh_2$, PPh_3, $P(4\text{-}FC_6H_4)_3$, $P[3,5\text{-}(CF_3)_2C_6H_3]_3$, $P(CH_2CH_2CN)_3$, $P(OMe)Ph_2$, $P(OMe)_2Ph$, $P(OMe)_3$, $P(OPh)_3$, and $P(OCH_2CF_3)_3$) has been prepared and the ^{195}Pt{^{1}H} and ^{31}P{^{1}H} NMR data obtained. These data have allowed us to expand the data base available for platinum(0) complexes and to draw empirical relationships from the platinum chemical shifts and platinum–phosphorus coupling constants.

Experimental Section

General Procedures. All reactions and sample preparations were carried out by use of standard Schlenk and inert-atmosphere-box techniques. Reagent grade solvents were dried by conventional methods[3] and distilled under argon. Distilled water and absolute ethanol were purged with an Ar stream for 20 min prior to use. Deuteriated THF, all phosphines and phosphites (all liquids were received under Ar) and $NaBH_4$ were used without further purification.

Synthesis of Complexes. The $Pt(tripod)PR_3$ complexes (PR_3 = $PPhMe_2$, PPh_2Me, PPh_3, $P(4\text{-}FC_6H_4)_3$, and $P(CH_2CH_2CN)_3$) were synthesized according to a published procedure.[4] The analogous phosphite complexes, $Pt(tripod)P(OR)_3$ ($P(OR)_3$ = $P(OMe)_3$, $P(OPh)_3$, and $P(OCH_2CF_3)_3$) were prepared by the same procedure; one must be careful to substitute the corresponding alcohol or THF for ethanol as the reaction solvent to prevent exchange of alkoxide groups. The complexes $Pt(tripod)P(OMe)Ph_2$ and $Pt(tripod)P(OMe)_2Ph$ were prepared in an NMR tube by adding the appropriate ligand ($P(OMe)Ph_2$ or $P(OMe)_2Ph$) to $Pt(tripod)PPh_2Me$ to displace PPh_2Me. The other complex, $Pt(tripod)P[3,5\text{-}(CF_3)_2C_6H_3]_3$, was prepared by refluxing a solution containing 0.2499 g (0.2806 mmol) of $PtCl_2(tripod)$ and 0.1885 g (0.2812 mmol) of $P[3,5\text{-}(CF_3)_2C_6H_3]_3$[5] in 35 mL of THF for 1 h. The resultant solution was concentrated to half its initial volume in vacuo; then 0.0341 g (0.830 mmol) of $NaBH_4$ dissolved in 10 mL of distilled water was added dropwise. The solvent was removed from the resulting orange slurry, and 20 mL of absolute ethanol and 10 mL of distilled water were added to the orange paste. The resultant orange solid was collected on a Schlenk frit, washed with 2 × 5 mL aliquots of distilled water, and dried in vacuo. Yield: 0.30 g.

Instrumentation. The ^{195}Pt{^{1}H} and ^{31}P{^{1}H} NMR spectra were recorded at 296 K on a Bruker MSL-300 spectrometer operating at 64.386 and 121.497 MHz, respectively. The ^{31}P{^{1}H} NMR spectra are referenced to external 85% H_3PO_4, and the ^{195}Pt{^{1}H} NMR spectra are referenced to external H_2PtCl_6 in D_2O/HCl with a correction made for the

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Table I. $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR Data for the Pt(tripod)PR$_3$ Complexes[a]

Pt(tripod)PR$_3$ no.	PR$_3$	δ(P1)	δ(P3)	δ(Pt)	^1J(Pt–P1)	^1J(Pt–P3)	^2J(P1–P3)	$\sum\chi_i$	cone angle[d]	σ^*
1	PMe$_2$Ph	−29.5	−14.2	−4809	5388	3070	51	9.5	122	0.6
2	PMePh$_2$	−2.8	−14.5	−4810	5388	3080	51	11.2	136	1.2
3	PPh$_3$	26.9	−14.3	−4781	5342	3099	51	12.9	145	1.8
4	P(4-FC$_6$H$_4$)$_3$[b]	24.0	−13.8	−4791	5456	3069	53	15.0	145	0.72
5	P(CH$_2$CH$_2$CN)$_3$[b]	13.9	−15.5	−4997	5486	2949	55	21.9	132	1.37
6	P[3,5-(CF$_3$)$_2$C$_6$H$_3$]$_3$	25.1	−15.5	−4898	5727	3001	57	NA[c]	NA	NA
7	P(OMe)Ph$_2$	121.0	−19.1	−4974	6300	2880	62	16.3	132	2.66
8	P(OMe)$_2$Ph	155.1	−16.0	−5060	7381	2865	71	19.7	115	3.51
9	P(OMe)$_3$	150.4	−18.1	−5273	8445	2885	77	23.1	107	4.37
10	P(OCH$_2$CF$_3$)$_3$	148.5	−16.5	−5372	8785	2805	85	NA	NA	NA
11	P(OPh)$_3$	116.4	−17.2	−5254	9128	2887	86	29.1	128	7.14

[a] Chemical shifts are in ppm; coupling constants are in Hz. [b] Saturated solutions, less than 0.05 M. [c] NA = not available. [d] In degrees.

THF-d_8 solvent. The chemical shifts obtained from the ^{195}Pt NMR spectra are accurate to ±0.1 ppm, and the coupling constants are accurate to ±5 Hz; for the $^{31}P\{^1H\}$ NMR spectra the chemical shifts are accurate to ±0.01 ppm, and the coupling constants are accurate to ±2 Hz. The samples were prepared in a 25/75 THF-d_8/THF solvent mixture as 0.05 M solutions, and spectra were recorded on samples in 10-mm NMR tubes fit with vortex plugs.

Discussion

^{195}Pt and ^{31}P Chemical Shifts. The Fourier transform $^{31}P\{^1H\}$ NMR spectra for the Pt(tripod)PR$_3$ complexes are first-order spectra as expected for an A_3MX spin system; they consist of a doublet with the corresponding ^{195}Pt satellites and a quartet with the corresponding ^{195}Pt satellites ($I = {}^1/_2$ for ^{195}Pt, 33.7% natural abundance). The $^{195}Pt\{^1H\}$ NMR spectra consist of a doublet of quartets. The data are compiled in Table I.

The main contribution to the net nuclear magnetic shielding (σ) of a heavy nucleus, σ_p, defined by Ramsey, can be expressed as[6,7]

$$\sigma_p = -e^2/(2m^2c^2)\sum_{n\neq 0}(E_n - E_o)^{-1}\{\langle o|\sum_j l_{\alpha j}|n\rangle\langle n|\sum_k r_k^{-3} l_{\alpha k}|o\rangle + \langle o|\sum_j r_j^{-3} l_{\alpha j}|n\rangle\langle n|\sum_k l_{\alpha k}|o\rangle\} \quad (1)$$

where e is the charge on an electron, m is the mass, c is the speed of light, o and n are the wave functions of the ground and excited states and E_o and E_n are the corresponding energies, l_α is the angular momentum operator for the jth electron and r_k is the distance of the kth electron from the nucleus under study. Thus, the ^{195}Pt chemical shift is affected by (1) the asymmetry of the electronic distribution within the 5d orbital of the platinum atom, (2) the mean inverse cube of the distance between these electrons and the platinum nucleus (r^{-3}), and (3) the inverse energy separations between the ground and excited states for these electrons ($[E_n - E_o]^{-1}$).[8]

The results of X-ray structural studies show that the tripod ligand appears to constrict the P–Pt–P angles to the range 93–99°;[9-12] hence, the Pt(tripod)PR$_3$ complexes possess pseudotetrahedral geometries. From the three factors listed above that affect the ^{195}Pt chemical shift, both the symmetry of the electronic distribution within the 5d orbitial and the mean inverse cube of the distance between these electrons and the platinum nucleus should remain fairly constant as the monodentate phosphine ligand is varied. Therefore, the ^{195}Pt chemical shifts should depend on the lowest available electronic excitation energy. In fact, the Pt(tripod)PR$_3$ complexes show a large chemical shift variation (range = 591 ppm) as the monophosphine ligand is varied.

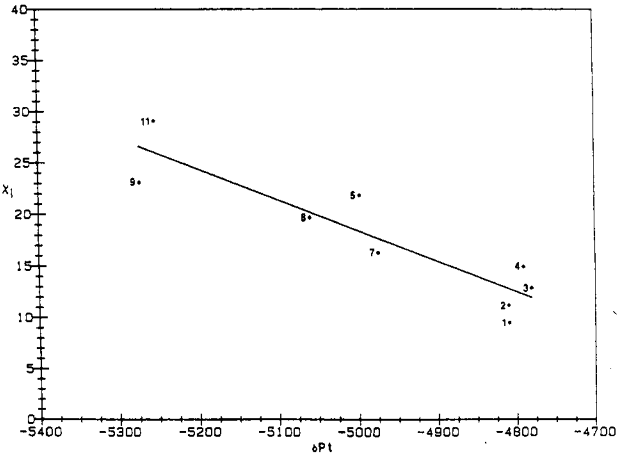

Figure 1. Plot of the sum of Tolman's substituent effect, $\sum\chi_i$, vs δ(Pt). The numbers on the plot correspond to the PR$_3$ ligands listed in Table I.

A rough linear correlation ($p = -0.905$) is observed between the ^{195}Pt chemical shift and the sum of the substituent contributions $(\sum\chi_i)^{13}$ of the groups bound to the monodentate phosphine ligand (Figure 1). The linear expression is given in eq 2. As

$$\sum\chi_i = -2.97 \times 10^{-2}(\delta(\text{Pt})) - 130 \quad (2)$$

the substituents bound to phosphorus become more electron withdrawing (larger $\sum\chi_i$) and the donor–acceptor ratio[14] of the PR$_3$ ligands decrease, δ(Pt) moves upfield; the apparent shielding becomes greater. This trend can be explained on the basis of a stronger Pt–P bond as the monodentate phosphine ligands become better π-acceptors. It should be noted that $\sum\chi_i$ takes into account only the electronic effect of the monophosphine ligand; however, the platinum resonance shifts downfield as the steric requirements of a phosphine ligand increases.[1] Therefore, a good correlation is not observed. A linear correlation, given in eq 3 with $p = -0.949$,

$$^1J(\text{Pt–P1}) = -6.75(\delta(\text{Pt})) - 2.72 \times 10^4 \quad (3)$$

is also observed between δ(Pt) and the one-bond, platinum–phosphorus coupling constant, ^1J(Pt–P1). The magnitude of the Pt–P1 coupling constant depends primarily on the percent s character present in the orbital containing the lone pair of electrons on phosphorus, α_p^2, and the valence s electron density at the nucleus, $|\psi_{3s}(0)|$.[2,4,15] The upfield shift of δ(Pt) with an increase in the magnitude of ^1J(Pt–P1) reflects a greater s character in the phosphorus orbital used for bonding to platinum.

The chemical shift values of Pt(II) complexes generally occur at higher fields than those of Pt(IV) complexes of comparable ligands, and the δ values of Pt(0) complexes have been reported in the same region as those for Pt(II) complexes.[1] However, if one combines older NMR data on Pt(0) complexes[8,16,17] with the

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data obtained in this study and those from recent published reports of Pt(0) chemical shifts,[18-22] we conclude that Pt(0) resonances generally occur at higher fields than those for Pt(II) complexes. Although Pt(II) complexes have ^{195}Pt resonances as high as −5500 ppm[1] (range for Pt(II) complexes: −1600 to −5500 ppm), the resonances of Pt(0) complexes occur as high as −6596 ppm[23] for $Pt[P(i\text{-}Pr)_3]_2$[18] (range for Pt(0) complexes: −4500 to −6600 ppm).

Coupling Constants ^1J(Pt–P1), ^1J(Pt–P3), and ^2J(P1–P3). Variation in the magnitudes of the Pt–P coupling constants for the tripod ligand, ^1J(Pt–P3), is relatively small as the monodentate phosphine ligand changes from PMe_2Ph to $P(OPh)_3$; however, the magnitude of the Pt–P coupling constant for the monodentate phosphine ligands, ^1J(Pt–P1), increases dramatically from 5342 to 9128 Hz. In addition, the magnitudes of ^1J(Pt–P3) are smaller than those observed for $Pt(PR_3)_4$ compounds.[24-26] These changes reflect the increased p character of the Pt–P3 bonds to the tripod ligand due to the constricted P3–Pt–P3 bond angles (93–99°). This constrained C_{3v} geometry of the tripod ligand allows a larger s character in the Pt–P1 bond; consequently, the P1 coupling constants are larger than for "T_d" Pt(0) complexes. As mentioned previously, the magnitude of the one-bond phosphorus coupling constant depends primarily on $\alpha_p{}^2$ and $|\psi_{3s}(P)|^2$. A change of the groups on one of the coupled phosphorus atoms (i.e., P1) can have a large effect on $\alpha_p{}^2$ and $|\psi_{3s}(0)|^2$ for that atom; however, it apparently has only a small effect on the corresponding terms of another phosphorus atom (i.e., P3).[27]

The magnitudes of ^1J(Pt–P) and ^2J(P–P) coupling constants for Pt(II) complexes are affected by the electronegativity of the phosphorus substituents.[28] This effect is observed also for the $Pt(tripod)PR_3$ complexes. A linear correlation ($p = 0.978$) is observed between ^2J(P1–P3) and Taft's constant[29]

$$\sigma^* = 1.57 \times 10^{-1}(^2J(\text{P1–P3})) - 7.10 \qquad (4)$$

A similar relationship has been observed for the one-bond, metal–phosphorus coupling constants, ^1J(Pt–P1), in related $Pt(tripod)PR_3$ complexes.[15] This similarity between ^2J(P1–P3) and ^1J(Pt–P1) is not surprising, since the two-bond, phosphorus–phosphorus coupling constants are transmitted through the metal center. In fact, a linear correlation ($p = 0.993$) exists between ^2J(P1–P3) and ^1J(Pt–P1) for the $Pt(tripod)PR_3$ complexes.

$$^2J(\text{P1–P3}) = 9.02 \times 10^{-2}(^1J(\text{Pt–P1})) + 3.85 \qquad (5)$$

Acknowledgment. The authors are grateful to the Amoco Foundation for a Graduate Fellowship to L.M.G. during 1986–1987, to Dr. Charles Cottrell for collecting the ^{195}Pt NMR spectra, and to The Ohio State University for a University Fellowship to L.M.G. and for purchase of the Bruker MSL-300 NMR spectrometer.

Registry No. **1**, 112712-94-4; **2**, 56261-12-2; **3**, 56261-10-0; **4**, 77933-86-9; **5**, 112712-95-5; **6**, 112712-96-6; **7**, 112712-97-7; **8**, 112712-98-8; **9**, 112712-99-9; **10**, 112713-00-5; **11**, 56261-15-5; $PtCl_2$(tripod), 112712-93-3; ^{195}Pt, 14191-88-9.

Supplementary Material Available: Sample $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ spectra and graphs corresponding to the least-squares equations (3)–(5) (5 pages). Ordering information is given on any current masthead page.

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Kinetics of the Displacement of Gadolinium(III) from a Water-Soluble Porphyrin by EDTA

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Received October 2, 1986

Paramagnetic water-soluble metalloporphyrins are being explored as tissue contrast agents in magnetic resonance imaging studies.[1,2] The tumor-concentrating ability[3,4] of tetrakis(4-sulfonatophenyl)porphyrin (H_2TPPS) combined with the f^7 configuration of gadolinium(III) provides an impetus for the study of GdTPPS. Aside from reconstitution of Yb–mesoporphyrin into myoglobin[5] and applications as NMR shift reagents,[6] most work on the lanthanide derivatives has involved water-insoluble porphyrins.[7-11] We report the kinetics of displacement of Gd^{3+} from GdTPPS by EDTA. This appears to be the first example of metal removal from a porphyrin by a chelating ligand.[12] The results parallel the kinetics of anion addition to certain cobalt(III) porphyrins.

Experimental Section

Gadolinium(III) was incorporated into H_2TPPS by the imidazole melt method, which we later found was similar to that described by Horrocks.[6] Two hundred milligrams (0.16 mM) of the sodium salt of $H_2TPPS\cdot 12H_2O$ was combined with 240 mg (0.65 mM) of $GdCl_3\cdot 6H_2O$ and 5.0 g of imidazole. The mixture under $N_2(g)$ was placed in an oil bath at 200 °C. Samples of the melt were periodically withdrawn, dissolved in water, and the spectrum monitored, when the 637-nm free-base peak disappeared, the porphyrin was removed from the oil bath, the bath temperature was lowered to 120 °C, and the bulk of the imidazole was sublimed away. The sample was cooled, washed with CH_2Cl_2, dissolved in a minimum amount of methanol containing 1% water, and precipitated by the addition of acetone. After three such precipitations, the compound in methanol was spotted on SiC_{18} Baker TLC plates, and developed with 90% methanol in water. Any free-base H_2TPPS moves with the solvent front, and GdTPPS has R_f 0.9. This band was cut from the plates, recovered in MeOH, evaporated under the hood, and finally dried at 40 °C. Anal. Calcd for $GdC_{44}N_4S_4O_{12}H_{24}Na_3\cdot 20H_2O$: Gd, 10.3; C, 34.88;

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