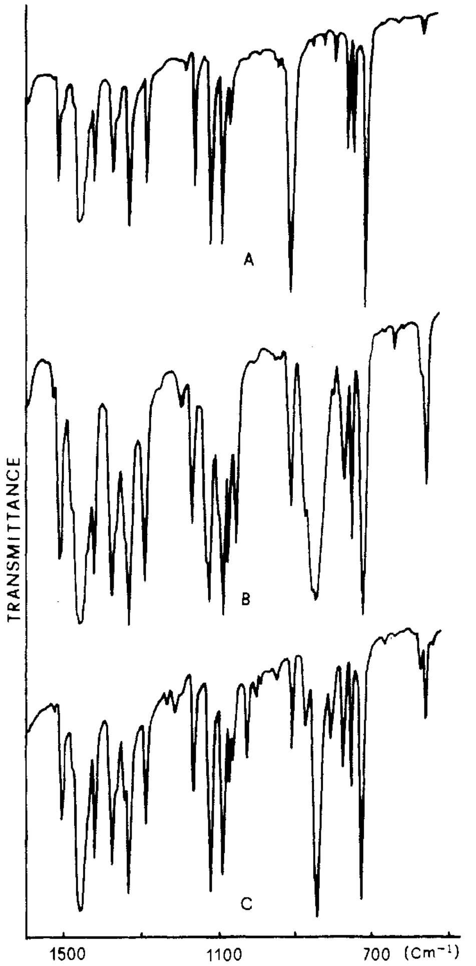

Figure 2. IR spectra of $(PcFe)_2N$ (A), $[(PcFe)_2N](PF_6)$ (B), and $[((py)PcFe)_2N](PF_6)$ (C).

complete disappearance of the signals present in the EPR spectrum of **3** ($g_\parallel = 2.03$, $g_\perp = 2.13$)[5] results from the oxidation to **5**, which is EPR silent, with the absence of even a trace of absorption at $g = 2$, as might be found for the formation of a phthalocyanine radical. A similar situation is found for the EPR spectra of **7–10**, indicating that there has been no substantial rearrangement of the charge distribution between the Fe–N–Fe moiety and the phthalocyanine ligands as a result of the ligation of the N-bases. In-plane location and six coordination for the Fe atoms in the N-base adducts **7–10** reiterate the closely resembling situation proposed for the corresponding μ-oxo adducts[4a] and very recently definitely established by X-ray work for the 1-Meim adduct, i.e. $((1\text{-Meim})PcFe)_2O$.[10] Species **7–10** appear to be unprecedented in the literature as solid, stable six-coordinate iron species among the few known μ-nitrido dimers formed with macrocyclic porphyrinlike systems.

Experimental Section

$(Fc)PF_6$. This ferrocenium salt was prepared by suspending ferrocene (10 g) for 5–6 h in a diluted aqueous solution of hydrochloric acid and hydrogen peroxide. The intensively blue solution obtained is then separated by the solid unreacted ferrocene by filtration, and an excess of ammonium hexafluorophosfate is added to it. The solid bluish $(Fc)PF_6$ formed is filtered, washed with methyl alcohol, and dried under vacuum (10^{-2} mmHg) (2.5 g). Anal. Calcd for $C_{10}H_{10}F_6FeP$: C, 36.5; H, 3.02. Found: C, 36.18; H, 3.02.

$(PcFe)_2N$ (3). Analytically pure samples of **3**, prepared by the method previously reported,[5] generally show room-temperature magnetic moments higher than 2.5–2.6 μ_B. Elimination of small amounts of paramagnetic impurities present in these samples can be obtained by oxidation of **3** to **5**, followed by the reverse process performed in the presence of piperidine and water (see below), with eventual duplication of the procedure. Reproducible, room-temperature magnetic moments of 2.13 ± 0.05 μ_B are obtained for the purified samples.

$((PcFe)_2N)PF_6$ (5). This complex can be obtained by suspending **3** (600 mg, 0.52 mmol) in a solution of $(Fc)PF_6$ (380 mg, 1.19 mmol) in acetone (200 mL) and stirring the reaction mixture at room temperature for 24 h. Solid crystalline **5** is separated by filtration from the solution, washed with acetone, and dried under vacuum (10^{-2} mmHg). The complex systematically shows the presence of water and acetone. It roughly analyzes for the formula $((PcFe)_2N)PF_6\cdot 2H_2O\cdot$acetone: Anal. Calcd for $C_{67}H_{42}N_{17}F_6Fe_2O_3P$: C, 57.90; H, 3.05; N, 17.13; Fe, 8.03. Found: C, 56.97; H, 3.27; N, 15.86; Fe, 8.33.

$[((4\text{-Mepy})PcFe)_2N]PF_6$ (7). This complex can be obtained by dissolving **5** (240 mg) in 4-Mepy (25 mL). The solution is kept for 30 min at room temperature. After filtration, ether is added to the solution to precipitate the complex. The solid formed is separated from the solution by filtration, washed with ether, and dried under vacuum (10^{-2} mmHg) (190 mg). Anal. Calcd for $C_{76}H_{46}F_6Fe_2N_{19}P$: C, 61.60; H, 3.13; N, 17.95. Found: C, 61.71; H, 3.36; N, 17.38.

$[((py)PcFe)_2N]PF_6$ (8). This adduct can be prepared as previously described.[5b] It can also be obtained by repeating twice the following procedure: **5** (270 mg) is dissolved in pyridine (15 mL) and the solution obtained is kept at room temperature for 30 min. After filtration, water is added to the solution to precipitate the complex, which is then separated, washed with water and 95% ethanol, and dried under vacuum (10^{-2} mmHg) (150 mg). Anal. Calcd for the formula $C_{74}H_{42}F_6Fe_2N_{19}P$: C, 61.14; H, 2.91; N, 18.30. Found: C, 61.34; H, 2.94; N, 18.0.

$[((pip)PcFe)_2N]PF_6$ (9). **5** (120 mg) is suspended in a mixture of ether (3–4 mL) and piperidine (0.7 mL) and the suspension stirred at room temperature for 2 h. After filtration, the solid material is washed with ether and dried under vacuum (10^{-2} mmHg). Anal. Calcd for the formula $C_{74}H_{54}F_6Fe_2N_{19}P$: C, 60.63; H, 3.71; N, 18.15. Found: C, 59.75; H, 3.59; N, 17.61. Addition of water to a solution of **5** in pure piperidine kept at room temperature for 30–40 min determines the formation of a precipitate that is identified as the μ-nitrido species **3**. Reiteration of the conversion of **3** into **5**, and reduction of the latter in pure piperidine, has allowed the purification of **3**, as indicated above for this complex.

$[((1\text{-Meim})PcFe)_2N]PF_6$ (10). A mixture obtained by suspending **5** (300 mg) in 1-Meim (15 mL) is kept under stirring at room temperature for 30-40 min. After filtration, ether is added to the solution and a precipitate is formed. The solid is separated from the solution by filtration, washed with ether, and dried under vacuum (10^{-2} mmHg). Anal. Calcd for the formula $C_{72}H_{44}F_6Fe_2N_{21}P$: C, 59.24; H, 3.04; N, 20.14. Found: C, 58.68; H, 3.32; N, 19.79.

Physical Measurements. IR spectra were recorded on a Perkin Elmer 983 spectrophotometer by using Nujol mulls and NaCl or CsI disks. EPR spectra were obtained on a Varian V 4502-4 spectrometer (X-band) at 110 K. Magnetic susceptibility measurements were obtained on a Gouy balance. Mössbauer spectra were obtained at 77 K on a conventional constant-acceleration spectrometer, which utilizes a room-temperature rhodium matrix cobalt-57 source. The spectra were fitted to Lorentzian line shapes by using a standard least-squares computer minimization technique.

Registry No. **3**, 98395-07-4; **5**, 111348-97-1; **7**, 111378-76-8; **8**, 98395-09-6; **9**, 111378-78-0; **10**, 111378-80-4.

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Ligand Substitution in (Ind)W(CO)$_3$Cl and (Ind)W(CO)$_3^-$Na$^+$ (Ind = Indenyl): Examples of Mixed Associative and Dissociative Substitution

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The greater reactivity of η^5-indenyl complexes of the transition elements when compared to their η^5-cyclopentadienyl analogues

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as received considerable recent attention.[1-3] Rates of ligand substitution can be as much as 10^8 times faster for indenyl complexes.[1a] This "indenyl effect" is often attributed to the ability of the indenyl ligand to promote associative processes by a ring-slippage mechanism,[3] but there has been little attention given to the ability of these ligands to promote dissociative substitution as well.[2] In the course of our studies of ligand substitution in 17-electron complexes of the group 6 metals,[4] we prepared (Ind)W(CO)$_3$Cl (Ind = η^5-C$_9$H$_7$) and observed its facile substitution chemistry. Herein we report our studies of ligand substitution in (Ind)W(CO)$_3$Cl and the related anion (Ind)W(CO)$_3^-$, examples where the indenyl effect promotes both associative and dissociative substitution.

Experimental Section

General Procedures and Instrumentation. All manipulations were carried out under an atmosphere of purified nitrogen or argon by using standard Schlenk or glovebox techniques and dried and degassed solvents. Infrared spectra were obtained on a Perkin-Elmer Model 781 spectrophotometer. NMR spectra were obtained on a Bruker AM-300 spectrometer. High-performance liquid chromatography (HPLC) was performed as described previously.[4b] NaInd (C_9H_7Na) was prepared from indene (Aldrich) and NaH in THF and stored as a pink solid. All solutions of **1**–**3** with phosphines or phosphites were protected from light.

(η^5-C$_9$H$_7$)W(CO)$_3$Cl (1). **1** was prepared from W(CO)$_6$ and NaInd by a modification of the method of Nesmeyanov.[1k] A solution of W(CO)$_6$ (5 g, 14.2 mmol) and NaInd (2.1 g, 15.2 mmol) in 100 mL of 1,4-dioxane was heated to 100 °C for 12 h. The solvent was removed in vacuo and the residue redissolved in 70 mL of degassed aqueous acetic acid (1.8 g, 30 mmol) at 0 °C. After 0.5 h the mixture was extracted with 100 mL of degassed toluene. The toluene extract was cooled to −15 °C and treated with 5 mL of CCl_4. The solution turned from yellow to orange-red immediately and finally to dark brown upon warming to room temperature. The solvent was removed in vacuo and the residue chromatographed on Florisil with CH_2Cl_2 as eluent to give 3.05 g (52%) of **1**. Recrystallization from CH_2Cl_2 at −40 °C gave large red crystals. IR (CH_2Cl_2): 2048 (s), 1962 (s), 1945 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): 5.63 (t, 1 H, J = 2.9 Hz), 5.92 (d, 2 H, J = 2.9 Hz), 7.42–7.52 ppm (m, 4 H). Anal. Calcd for $C_{12}H_7ClO_3W$: C, 34.44; H, 1.69; Cl, 8.47. Found: C, 34.21; H, 1.94; Cl, 8.60.

(η^5-C$_9$H$_7$)W(CO)$_2$(PPh$_3$)Cl (2). A solution of 150 mg (0.36 mmol) of **1** dissolved in a minimum of acetonitrile was allowed to stand at −30 °C overnight. This yielded dark burgundy-colored crystals of (Ind)W(CO)$_2$(CH$_3$CN)Cl (114 mg, 74%); mp 100 °C dec. IR (CH_3CN): 1952 (s), 1868 (s) cm^{-1}. Without further purification, 100 mg (0.232 mmol) of (Ind)W(CO)$_2$(CH$_3$CN)Cl in 20 mL of CH_2Cl_2 was treated with a slight excess of PPh$_3$ (64 mg, 0.244 mmol) at room temperature. Recrystallization from toluene at −30 °C gave 104 mg (69%) of orange-red crystals of **2**; mp 190 °C dec. IR (CH_2Cl_2): 1955 (s), 1869 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): 5.25 (m, 1 H), 5.38 (t, 2 H, J = 2.7 Hz), 7.1–7.4 ppm (m, 19 H). Anal. Calcd for $C_{29}H_{22}ClO_2PW$: C, 53.36; H, 3.40; P, 4.75; Cl, 5.43. Found: C, 53.38; H, 3.56; P, 4.54; Cl, 5.68.

Table I. Crystal Data for (Ind)W(CO)$_3$Cl (**1**) and (Ind)W(CO)$_2$(PPh$_3$)Cl (**2**)

mol formula	$C_{12}H_7ClO_3W$	$C_{29}H_{22}ClO_2PW$
fw	418.47	652.76
cryst size, mm	0.18 × 0.38 × 0.15	0.4 × 0.2 × 0.2
cryst color	red	orange
space group	Pc, pseudo-$P2_1/c$	$P2_1/c$
a, Å	7.468 (2)	17.544 (4)
b, Å	12.169 (3)	14.728 (3)
c, Å	13.081 (3)	9.765 (2)
β, deg	91.62 (2)	104.23 (2)
V, Å^3	1188	2446
Z	4	4
d, g/cm^3	2.34	1.77
μ(Mo Kα), cm^{-1}	101.5	50.2
abs cor	yes	yes
max, min, av	0.293, 0.163, 0.245	1.216, 0.833, 0.995
scan range (2θ), deg	4–50	4–54
no. of reflcns measd	4370	5513
no. of unique data	2194	5382
no. of data with $F > 3\sigma(F)$	1323	3467

Table II. Fractional Coordinates and Isotropic Thermal Parameters[a] for (Ind)W(CO)$_2$(PPh$_3$)Cl

	10^4x	10^4y	10^4z	$10B$, Å^2
W(1)	3678.3 (2)	633.2 (2)	1408.8 (3)	25.06 (4)
Cl(1)	3613 (1)	−646 (1)	−286 (2)	38.3 (4)
P(1)	2227 (1)	300 (1)	728 (2)	22.8 (3)
O(10)	4319 (3)	1626 (5)	−865 (6)	59 (2)
O(11)	3044 (3)	2597 (4)	1076 (6)	49 (1)
C(1)	4723 (5)	1091 (6)	3160 (8)	40 (2)
C(2)	4068 (5)	950 (6)	3776 (8)	40 (2)
C(3)	3938 (4)	8 (5)	3816 (7)	33 (2)
C(4)	3435 (5)	539 (6)	4432 (8)	44 (2)
C(5)	3484 (5)	−1450 (7)	4364 (9)	53 (2)
C(6)	3996 (5)	−1885 (6)	3670 (9)	53 (2)
C(7)	4478 (5)	−1406 (6)	3036 (8)	44 (2)
C(8)	4471 (4)	−439 (5)	3139 (7)	34 (2)
C(9)	4929 (4)	242 (6)	2659 (8)	38 (2)
C(10)	4066 (4)	1232 (5)	−52 (8)	37 (2)
C(11)	3262 (4)	1865 (5)	1223 (7)	34 (2)
C(21)	1787 (4)	214 (5)	−1157 (6)	27 (1)
C(22)	2112 (4)	687 (5)	−2105 (7)	36 (2)
C(23)	1774 (5)	641 (7)	−3526 (8)	47 (2)
C(24)	1105 (6)	134 (6)	−4024 (8)	53 (2)
C(25)	771 (5)	338 (6)	−3118 (9)	47 (2)
C(26)	1115 (4)	300 (5)	−1678 (7)	34 (2)
C(31)	1599 (4)	1134 (4)	1331 (7)	25 (1)
C(32)	360 (4)	1349 (5)	511 (7)	29 (1)
C(33)	391 (4)	1951 (6)	1047 (8)	37 (2)
C(34)	643 (4)	2320 (6)	2347 (8)	39 (2)
C(35)	1382 (4)	2103 (6)	3163 (7)	39 (2)
C(36)	1862 (4)	1522 (5)	2646 (7)	32 (1)
C(41)	1919 (4)	−747 (5)	1442 (6)	27 (1)
C(42)	1443 (5)	−734 (5)	2385 (8)	40 (2)
C(43)	1246 (5)	−1541 (6)	2967 (8)	47 (2)
C(44)	1504 (5)	2342 (6)	2642 (6)	46 (2)
C(45)	1958 (5)	2372 (6)	1645 (9)	46 (2)
C(46)	2177 (4)	1578 (5)	1068 (8)	38 (2)

[a] Isotropic values for those atoms refined anisotropically are given by $(4/3)(a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3))$.

Kinetic Studies. In a typical experiment a solution of PPh$_3$ in 10 mL of toluene was added to a 10-mL solution of **1** after both solutions had been held at 15 °C for 30 min. Reaction solutions were 2.5×10^{-3} M in the metal complex and 0.05–0.45 M in ligand. Aliquots were removed periodically for analysis by HPLC. Values of k_{obsd} were obtained from plots of $-\ln([\mathbf{1}]_t/[\mathbf{1}]_0)$ vs time. All plots were linear for at least 3

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Table III. Calculated Values of k_a and k_d for the Reactions of **1**, **3**, and $(Ind)Mo(CO)_3X$ (X = Cl,Br,I) with PPh_3 and $P(OPh)_3$

complex	ligand	solvent/temp °C	k_d, 10^{-4} s^{-1}	k_a, 10^{-4} M^{-1} s^{-1}	k_a/k_d	ref
1	PPh_3	TOL/15	9.20	401	44	*a*
3	$P(OPh)_3$	THF/30	4.51	112	25	*a*
$(Ind)Mo(CO)_3Cl$	PPh_3	THF/10	65.3	10.7	0.17	2a
$(Ind)Mo(CO)_3Br$	PPh_3	THF/15	7.60	5.3	0.68	2a
$(Ind)Mo(CO)_3I$	$P(OPh)_3$	THF/30	1.77	0.24	0.14	2a

[a] This work.

half-lives. Kinetic measurements under a CO atmosphere were performed in a like manner using CO-saturated solutions that were degassed by three freeze–thaw cycles.

The complex $(Ind)W(CO)_3^-Na^+$ (**3**) was generated by stirring a solution of **1** in THF over Na/Hg amalgam for 5 h, followed by filtration of the solution. Formation of **3** was confirmed by a subsequent IR spectrum, and **3** was used without further purification. IR (THF): 1898 (s), 1796 (s), 1745 (s) cm^{-1}. Kinetic studies were performed as above by monitoring the disappearance of the band at 1745 cm^{-1}. First-order plots of –ln [**3**] vs time were linear for greater than 3 half-lives although significant amounts of products other than $(Ind)W(CO)_2(PPh_3)^-$ were observed.

X-ray Crystallography. Suitable crystals of **1** and **2** were obtained by crystallization from CH_2Cl_2 and toluene, respectively. Although both compounds gave adequate diffraction data, only **2** could be refined to an acceptable level. Crystal data for both compounds are given in Table I, and non-hydrogen positional parameters for **2** are given in Table II. The structure solution was performed by the Patterson method in both cases. Full-matrix least-squares refinement for **2**, treating all non-hydrogen atoms anisotropically and using calculated positions for isotropic hydrogen atoms, led to final values of $R = 0.029$ and $R_w = 0.039$. The structure of **1** was pseudocentrosymmetric, and refinement was carried out in both $P2_1/c$ and Pc space groups. Strong correlations between parameters prompted us to use damping and a rigid-body model for the six-membered ring. Nevertheless, a unique solution was not found. Refinement of the centrosymmetric model converged at $R = 0.065$ and $R_w = 0.092$, whereas the noncentrosymmetric model converged at $R = 0.019$ and $R_w = 0.022$. Additional details for both structures are given in the supplementary material.

Results

Kinetics Studies. $CpW(CO)_3Cl$, like the majority of 18-electron metal carbonyls,[5] undergoes thermal ligand substitution by a sluggish dissociative pathway.[6] Reasonable rates of substitution can only be achieved at temperatures well above ambient, and acceleration by added ligand is not observed. By comparison, treatment of $(Ind)W(CO)_3Cl$ (**1**) with a variety of ligands rapidly gives the product of substitution even at temperatures below ambient. An examination of the kinetics of this reaction reveals mixed unimolecular and bimolecular processes. A plot of the pseudo-first-order rate constants k_{obsd} vs $[PPh_3]$ at 15 °C in toluene solvent is given in Figure 1. These data fit the two-term expression eq 1, and values of k_a and k_d are given in Table III.

$$k_{obsd} = k_d + k_a[L] \qquad (1)$$

In an effort to confirm the dissociative nature of the unimolecular process, we examined the reaction under an atmosphere of carbon monoxide. To our surprise dissolved CO had the effect of increasing, not decreasing, the rate of substitution (Figure 1). Although the intercept extrapolated from the rate data at low phosphine concentrations is nearly zero (-1.0×10^{-5} s^{-1}), as expected for CO inhibition, the data are not linear throughout. Moreover, the values of k_a thus calculated is greater than, not equal to, k_a observed in the absence of CO. These data do not fit a simple rate expression such as eq 1, and we do not have a convincing explanation for this curious behavior. We note, however, that carbon monoxide can be a reasonable nucleophile and propose that phosphine may be capturing an $(\eta^3\text{-Ind})W(CO)_4Cl$ intermediate.[4,7]

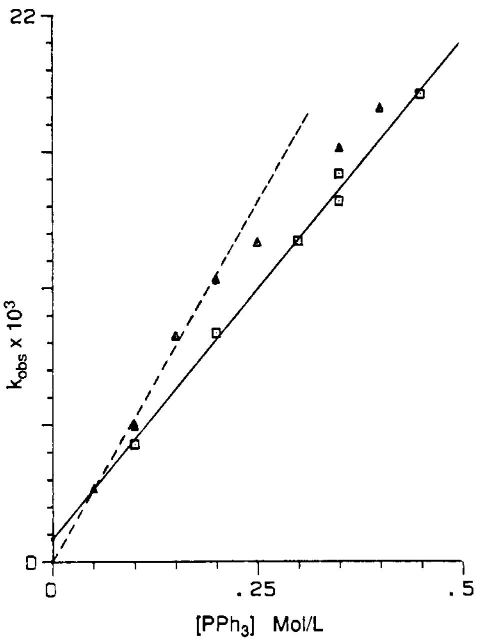

Figure 1. Pseudo-first-order rate constants k_{obsd} vs $[PPh_3]$ for $(Ind)W(CO)_3Cl$ (**1**) under argon (□) and under 1 atm of CO (△) at 15 °C in toluene.

The reaction of **1** with PPh_3 is clean, giving *cis*-$(Ind)W(CO)_2(PPh_3)Cl$ (**2**) as the only product under both a nitrogen and CO atmosphere. The stereochemistry assigned to the observed product is consistent with its IR and NMR spectra and was confirmed by a subsequent X-ray crystal structure analysis.

The complex $(Ind)W(CO)_3^-Na^+$ (**3**) can readily be prepared by reduction of **1** with Na/Hg amalgam in THF and identified by its characteristic infrared spectrum. **3** reacts sluggishly with phosphines and phosphites to give $(Ind)W(CO)_2(PR_3)^-$ as the initial product but rapidly reacts with excess ligand, displacing the indenyl ligand altogether.[8] At lower phosphine concentrations, treatment of these reactions solutions with CCl_4 leads to isolation of $(Ind)W(CO)_2(PR_3)Cl$ in moderate yield. Of most interest is the observation that a plot of k_{obsd}, obtained from the disappearance of **3** at 30 °C, vs $[P(OPh)_3]$ is linear; calculated values of k_a and k_d are given in Table III. Thus, substitution occurs by mixed associative and dissociative pathways in **3**, and the effect of increasing the molecular charge is to decrease the rate of both pathways.

Structural Studies. We examined the structures of both $(Ind)W(CO)_3Cl$ (**1**) and *cis*-$(Ind)W(CO)_3(PPh_3)Cl$ (**2**) by X-ray crystallography for evidence of distortion of the metal–ligand bonding. Only for the structure of **2** did refinement converge satisfactorily. A drawing of **2** along with selected bond distances and angles is given in Figure 2. The structure of **2** can be described as a four-legged piano stool with the electronegative chlorine atom oriented toward the arene portion of the indenyl ligand. The four ligands that constitute the legs of the stool are somewhat pinched with the trans Cl–M–CO angle (133.4°) larger than the trans P–M–CO angle (114.2°). In addition, there is evidence of ring slippage in the metal–indenyl ligand bonding. To use the slip parameters of Faller, Crabtree, Habib,[9] the W

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(8) Similar behavior was observed by Mawby in several cases.[2a,6]

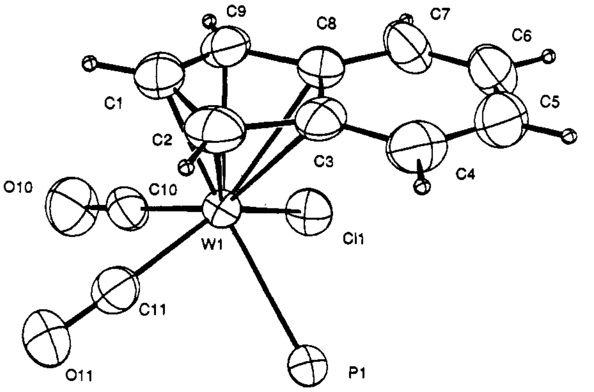

Figure 2. Molecular structure and labeling scheme (50% probability) of (Ind)W(CO)$_2$PPh$_3$Cl (**2**). Selected bond lengths (Å): W–C(1) = 2.279 (6); W–C(2) = 2.291 (7); W–C(3) = 2.469 (6); W–C(8) = 2.476 (7); W–C(9) = 2.307 (6); W–P = 2.516 (1); W–Cl = 2.492 (2); W–C(10) = 1.936 (7); W–C(11) = 1.947 (7). Selected bond angles (deg): P–W–C(11) = 79.9 (2); P–W–Cl = 78.38 (5); C(10)–W–C(11) = 72.5 (3); Cl–W–C(10) = 79.7 (2).

atom has slipped a distance $|S| = 0.132$ Å away from the centroid along a vector $\alpha = 34°$ relative to the centroid–C(1) axis; the difference between the mean W to C(2), C(1), and C(9) distance and the mean W to C(3) and C(8) distance is $\Delta(\overline{\text{W–C}}) = 0.14$ Å, and the dihedral angle between the plane of C(2)–C(1)–C(9) and the best-fit plane of C(2)–C(3)–C(8)–C(9) is $\Omega = 7.6°$. These values differ only slightly from the values of $|S| = 0.138$ Å, $\alpha = 79°$, $\Delta(\overline{\text{Mo–C}}) = 0.11$ Å, and $\Omega = 9.6°$ obtained from the structure of (Ind)Mo(CO)$_3$I by Mawby and Pringle.[10]

Discussion

Ligand substitution in (Ind)W(CO)$_3$Cl (**1**) is orders of magnitude faster than in the parent CpW(CO)$_3$Cl and occurs by competitive associative and dissociative pathways. Thus, in addition to the expected promotion of the associative mechanism, the indenyl ligand has also enhanced the rate of ligand dissociation in **1**. To a lesser extent the same is true of **3**.

Ligand substitution is also faster in **1** than in the isostructural Mo compounds (Ind)Mo(CO)$_3$X (X = Cl, Br, I) studied by Mawby.[2] The difference is largely in the associative pathway. Associative substitution by PPh$_3$ is approximately 37 times faster in **1** than in (Ind)Mo(CO)$_3$Cl under comparable conditions, whereas the dissociative pathway is in fact faster in the Mo complex. Some pertinent data are summarized in Table III. This difference is most evident in a comparison of the rate constant ratio k_a/k_d. The ratio k_a/k_d is consistently less than 1.0 for the reaction of the Mo complexes with PPh$_3$ but large for reaction of **1** with PPh$_3$ and **3** with P(OPh)$_3$. Even the most nucleophilic ligand employed by Mawby, PBu$_3$, only achieved a ratio of $k_a/k_d = 15.1$.

The associative pathway appears to be more strongly influenced by the steric bulk of the entering ligand than by its electron-donor properties. Associative substitution in both **1** and **3** is much faster with the smaller P(OPh)$_3$ (cone angle $\theta = 128°$) than for the more basic but larger PPh$_3$ ($\theta = 145°$).[11] Similarly, the reactivity order observed for (Ind)Mo(CO)$_3$Br was PBu$_3$ > P(OMe)$_3$ > PPh$_3$ > P(OPh)$_3$.[2] It is unlikely that this steric argument can account for the difference in the ease of the associative pathway between (Ind)Mo(CO)$_3$X and **1** as the average metal-to-carbon bond distances are virtually identical.

Electronic effects are known to strongly influence the rates of associative substitution. For example, Rerek and Basolo observed that substitution by PPh$_3$ in the electron-deficient (η^5-C$_5$H$_4$NO$_3$)Rh(CO)$_2$ is 10^4 times faster than in (η^5-C$_5$H$_5$)Rh(CO)$_2$.[1a] Conversely, we observe that both associative substitution and dissociative substitution are much slower in the anion (Ind)W(CO)$_3^-$ than in neutral (Ind)W(CO)$_3$Cl. On the other hand, the infrared spectra of (Ind)Mo(CO)$_3$Cl and **1** differ only slightly and oppositely to their observed difference in reactivity.[12] Similar, spectroscopic measures of the electron density at the metal center differ only slightly for η^5-indenyl and η^5-cyclopentadienyl complexes. Ground-state electronic-effects do not account for the indenyl effect.

If significant steric and electronic differences between indenyl and cyclopentadienyl complexes do not exist and similar differences do not exist between (Ind)Mo(CO)$_3$Cl and **1**, then what can account for the extraordinary effect of indenyl ligands on the rates of substitution? In the absence of ground-state effects, this phenomenon must be associated with the ability of the indenyl ligand to accommodate changes in electron density and bonding in the transition state for substitution. In our work and that of Mawby,[4] it is established that the indenyl effect can strongly influence both dissociative and associative substutution pathways. Yet, the oft-cited ring-slippage mechanisn can at best aid an associative pathway. It is more likely that both the greater polarizability of the π-electrons of the arene system and the ability of the indenyl ligand to distort structurally contribute to the unique ability of this ligand to facilitate diverse reaction pathways.

Registry No. **1**, 68643-48-1; **2**, 112068-64-1; **3**, 112022-01-2; (Ind)W(CO)$_2$(CH$_3$CN)Cl, 112022-02-3; W(CO)$_6$, 14040-11-0; NaInd, 23181-84-2.

Supplementary Material Available: Tables of kinetics data for the reactions of **1** and **3**, tables of crystallographic data, complete positional and thermal parameters, and bond distances and angles for **1** and **2**, ORTEP drawings of **1** and **2**, and a figure showing the atom-numbering scheme in **2** (26 pages); lists of observed and calculated structure factors (52 pages). Ordering information is given on any current masthead page.

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(12) The IR absorptions reported for (Ind)Mo(CO)$_3$Cl at 2063, 1995, and 1963 cm^{-1} in CHCl$_3$[2d] are at higher energy than those for **1**. Thus substitution in the Mo complex should be faster, contrary to observation.

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N-Protonations and N-Alkylation of Cyclenphosphorane. Synthesis and Crystal Structure of a Stable Phosphorus Compound with Two N-Protonated P–N Bonds

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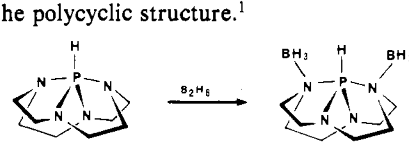
We recently reported that cyclenphosphorane (**1**) reacts with diborane to afford cyclenphosphorane–bis(borane) (**2**), revealing the unexpectedly strong basicity of the P-bonded apical nitrogen atoms in the polycyclic structure.[1]



1 **2**

The isolation of **2** raised the following questions: What will be the direct action of a protic acid on **1** (P–N bond cleavage, alteration of the tetracyclic structure)? If not, how many nitrogen atoms can one protonate on **1**? Can the equatorial nitrogen atoms be protonated?

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