reductive coupling of pyridine ligands through the 4-position in the intermediate Ti(II) complex.[14] This results in a final oxidation state of 3+ for the titanium atoms in **3**. The much shorter distance to the reduced pyridine ring nitrogen is consistent with the resulting amido linkage.

The use of the more redox stabilizing 2,2′-bipyridyl (bipy) ligand allows the isolation of the more soluble deep blue-green derivative $Ti(OAr\text{-}2,6\text{-}i\text{-}Pr_2)_2(bipy)_2$ (**4**) directly from **2** (Scheme I).[15] An X-ray diffraction study of **4**[16] confirms the stoichiometry and shows the aryloxide ligands to be mutually cis (Figure 3). Electrochemical studies of **4** show the presence of two one-electron oxidations at −0.95 and −0.07 V as well as a one-electron reduction at −1.51 V. All three waves appear to be reversible as judged by the ratio's $I_a/I_c = 1$. indeed, bulk electrochemical oxidation at −0.75 V generates stable, olive-green solutions of the monocation $[Ti(OAr\text{-}2,6\text{-}i\text{-}Pr_2)_2(bipy)_2]^+$ [18] which exhibits an identical cyclic voltammogram to solutions of **4** except that the wave at −0.95 V is now a reduction. However, attempts to generate solutions of the ions $[Ti(OAr\text{-}2,6\text{-}i\text{-}Pr_2)_2(bipy)_2]^{2+}$ and $[Ti(OAr\text{-}2,6\text{-}i\text{-}Pr_2)_2(bipy)_2]^-$ by bulk electrochemical oxidation at +0.0 V and reduction at −1.7 V led to solutions having broad cyclic voltammograms with no relationship to those of **4**. The electrochemical and spectroscopic properties so far examined for **4** are consistent with its formulation as containing a Ti(II) metal center and against an alternate formulation as $[Ti(OAr\text{-}2,6\text{-}i\text{-}Pr_2)_2(bipy^-)(bipy)]$ although further studies are presently underway on **4** and other related derivatives to more fully establish this point.

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Supplementary Material Available: Tables of atomic coordinates, temperature factors, and bond distances and angles (40 pages); tables of observed and calculated structure factors (47 pages). Ordering information is given on any current masthead page.

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(13) Crystal data for $Ti_2O_4N_6C_{78}H_{98}$ (**3**) at −156 °C: space group $P\bar{1}$, $a = 14.557$ (7) Å, $b = 13.155$ (7) Å, $c = 11.507$ (6) Å, $\alpha = 101.83$ (2)°, $\beta = 86.02$ (2)°, $\gamma = 107.86$ (2)°, $Z = 1$, $d_{calcd} = 1.035$ g cm^{-3}. Of the 5402 unique reflections collected by using Mo Kα radiation, $6° \leq 2\theta \leq 45°$, the 2777 were used in the final refinement. Final residuals are $R = 0.0789$, $R_W = 0.0826$. A disordered molecule of solvent was located in the unit cell, but it proved impossible to identify its chemical nature.

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(15) To a solution of **2a** (0.43 g, 0.58 mmol) in benzene (30 mL) was added 2 equiv of bipy (0.18 g, 1.2 mmol). The solution rapidly turned from red-brown in color to dark blue-green. After 30 min the solvent was removed in vacuo, and the remaining solids were washed with hexane. Yield = 0.33 g (80%). Quality crystals were obtained from toluene on slow cooling. Anal. Calcd for $TiC_{44}H_{50}O_2N_4$: C, 73.93; H, 7.05; N, 7.84. Found: C, 72.33; H, 7.21; N, 7.31.

(16) Crystal data for $TiO_2N_4C_{44}H_{50}$ (**4**) at 22 °C: space group $P\bar{1}$, $a = 13.102$ (4) Å, $b = 16.328$ (4) Å, $c = 19.726$ (3) Å, $\alpha = 102.57$ (2), $\beta = 96.54$ (2), $\gamma = 102.06$ (2), $Z = 4$, $d_{calcd} = 1.195$ g cm^{-3}. A total of 10 347 unique data were collected with Mo Kα $4° \leq 2\theta \leq 45°$ of which 5767 with $F > 3\sigma(F)$ were used in the refinement. Two similar but independent molecules were found in the unit cell. The data reported here is for the present state of refinement with only the central coordination sphere anisotropic giving residuals of $R = 0.089$ and $R_W = 0.122$. Further refinement is presently underway.

(17) Cyclic voltammograms and bulk electrochemistry were performed by using a Bioanalytical Systems Inc. Model CV-27 instrument, a three compartment H-cell, 0.2 M $n\text{-}Bu_4N^+PF_6^-$/THF solvent, Pt-disk or gauze electrode, and a Ag/AgCl quasi-reference electrode against which the Cp_2Fe/Cp_2Fe^+ couple lies at +0.47 V.

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Coordination Chemistry at the Carbide Heteroatom in a Metal Cluster. Synthesis, Structure, and Bonding for $[PPN][Fe_2Co(CO)_9(CPMe_3)]$

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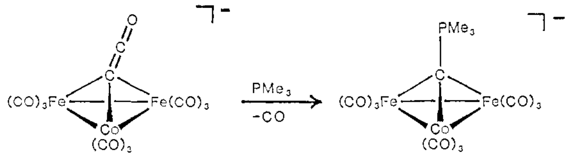
Ligand substitution reactions at metal centers are of fundamental importance in organometallic chemistry and have numerous applications to synthesis and homogeneous catalysis.[1] Main group elements in metal clusters can support a variety of ligands, thus providing the potential for new chemistry involving ligand substitution at nonmetal sites. To date, however, facile substitution reactions of this type have been rare.[2] In the present communication, we describe unprecedented reactions in which either CO or H coordinated to carbon in a three-metal cluster are displaced by a nucleophile, trimethylphosphine.

Treatment of $[PPN][Fe_2Co(CO)_9(CCO)]$ (**1**) (PPN = bis(triphenylphosphine)iminium cation) with 1 equiv of PMe_3 in CH_2Cl_2 at room temperature generates $[PPN][Fe_2Co(CO)_9(CPMe_3)]$ (**2**) within 30 min, while liberating 1 equiv of CO, eq 1. Moderately air-stable, red-brown crystals of **2** are obtained from CH_2Cl_2/Et_2O/pentane in 86% yield.[3] The solution IR spectrum of **2** contains an intense ν_{CO} band at 1952 cm^{-1}, almost 50 cm^{-1} below that of **1** and near the ν_{CO} of comparable dinegatively charged clusters.[4,5] The ^{13}C NMR spectrum of **2** contains a doublet centered at 203.3 ppm ($^1J_{PC} = 33.5$ Hz) assigned to the capping carbon atom. The replacement of CO by a phosphine at the carbon center of a cluster has not been previously observed, but an analogous reaction at boron has been reported for $H_3Os_3(CO)_9(BCO)$.[2] When the reaction of **1** with PMe_3 is monitored by NMR spectroscopy, it is found that the substitution reaction occurs by initial attack at the metal framework,[6] forming $[Fe_2Co(CO)_8(PMe_3)(CCO)]^-$. The large line width of the signal in the ^{31}P NMR spectrum suggests that PMe_3 is attached to Co. All attempts to isolate this intermediate species have failed.



1 2 (1)

The structure of **2** was determined by single-crystal X-ray diffraction,[7] Figure 1. The μ_3-$CPMe_3$ ligand forms an essentially symmetric cap on the three metal atoms, and the PMe_3 moiety orients in a staggered conformation with respect to the triangular

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(1) (a) Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: 1980. (b) Parshall, G. *Homogeneous Catalysis*; Wiley-Interscience: 1980.

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(3) **2**: IR ν_{CO} (CH_2Cl_2) 2023 (w), 1988 (m), 1952 (s), 1901 (m) cm^{-1}; ^1H NMR (CD_2Cl_2, +25 °C) 1.84 (d, $^2J_{PH} = 11.9$ Hz) ppm; ^{31}P NMR (CD_2Cl_2, +25 °C) 24.6 (s) ppm; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −90 °C) 217.1 (s, CO), 203.3 (d, $^1J_{PC} = 33.5$ Hz, C–$P(CH_3)_3$) ppm. Anal. Calcd for $C_{49}H_{39}O_9P_3NFe_2Co$: C, 56.08; H, 3.72; P, 8.86. Found: C, 55.96; H, 3.57; P, 9.04.

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(5) Ching, S.; Holt, E. M.; Kolis, J. W.; Shriver, D. F., manuscript in preparation.

(6) $[PPN][Fe_2Co(CO)_8(P(CH_3)_3)(CCO)]$: ^1H NMR (CD_2Cl_2, −90 °C) 1.37 (d, $^2J_{PH} = 8.6$ Hz) ppm; ^{31}P NMR (CD_2Cl_2, −90 °C) 2.0 (s, br) ppm; ^{13}C NMR (CD_2Cl_2, −90 °C) 216.1 (s, CO), 177.1 (d on s, $^1J_{CC} = 73.3$ Hz, CCO), 86.4 (br, CCO) ppm.

(7) Crystallographic data: $C_{49}H_{39}NO_9P_3Fe_2Co$, $M_r = 1049.4$; monoclinic, space group $P2_1/c$ (no. 14); $a = 14.370$ (3) Å, $b = 18.761$ (2) Å, $c = 17.621$ (3) Å, $\beta = 94.21$ (2)°, $V = 4738$ (2) Å^3; $Z = 4$, $D_{calcd} = 1.47$ g·cm^{-3}; μ(Mo Kα) = 11.4 cm^{-1}. The structure was solved by direct methods in SDP (B. A. Frenz and Assoc., College Station, TX, and Enraf-Nonius, Delft, Holland, 1985) and refined by using TEXSAN 2.0 (Swepston, P. N. Molecular Structure Corporation, College Station, TX, 1986). Full-matrix least-squares refinement gave $R(F) = 0.034$ and $R_w(F) = 0.046$ for 5969 reflections with $F^2 \geq 3\sigma(F^2)$ measured up to $2\theta = 50°$ at −120 °C (Mo Kα radiation, $\lambda = 0.71069$ Å).

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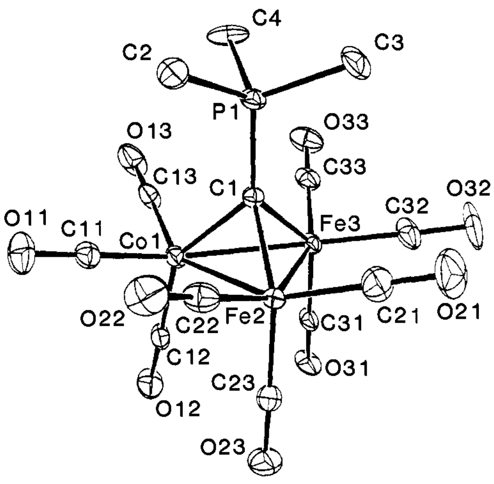
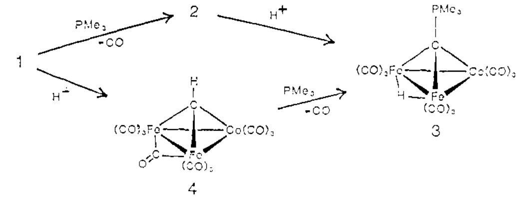


Figure 1. An ORTEP drawing of $[Fe_2Co(CO)_9(CPMe_3)]^-$. Some selected bond distances (Å): Col–Fe2 = 2.5460 (7), Col–Fe3 = 2.5332 (6), Fe2–Fe3 = 2.5567 (8), Col–Cl = 1.914 (3), Fe2–Cl = 1.934 (3), Fe3–Cl = 1.903 (3), Cl–Pl = 1.715 (3), av Pl–CH_3 = 1.792 (3).

Scheme I



face. The Cl–Pl distance, 1.715 (3) Å, is significantly shorter than the three equivalent Pl–CH_3 distances (av 1.792 (3) Å). In comparison to organic and organometallic phosphorus ylides,[8] the Cl–Pl distance is longer than the C=P bond of $Ph_3P{=}CH_2$ (1.661 (8) Å)[9] but shorter than or similar to the C=P bonds of phosphorus ylides bridging two metal centers (1.750(18) – 1.82(4) Å).[10–13]

Compound **2** does not react further with excess PMe_3 and cannot be reconverted to **1** under CO. Protonation of **2** using HSO_3CF_3 occurs across the Fe–Fe bond, giving $HFe_2Co(CO)_9(CPMe_3)$ (**3**).[14] Compound **3** can also be generated from the reaction of $Fe_2Co(CO)_{10}(\mu_3\text{-}CH)$ (**4**)[15] with PMe_3, a reaction in which the phosphine induces C–H bond cleavage. The reaction of **4** with PMe_3 was monitored by ^1H, ^{13}C, and ^{31}P NMR spectroscopies and initially gave spectra which suggested the formation of numerous intermediates. Nonetheless, **3** is produced cleanly upon completion of the reaction. Scheme I summarizes the reactions described above.

Compound **1** can be viewed as a heteroatomic carbonyl cluster based on a pseudotetrahedral M_3C core. This treatment of **1** is in accordance with the valence formalisms of Wade[16] and Mingos.[17] In addition, an analogy is evident between eq 1 and ligand substitution reactions of tetranuclear metal carbonyl clusters. Indeed, **1** and a four-metal analogue, $[Fe_4(CO)_{13}]^{2-}$, exchange all CO ligands with ^{13}CO gas at a comparable rate.[5,18] Despite the ease with which **2** is formed, phosphine substitution for CO at the carbon vertex of $M_3(CO)_9(CCO)$ clusters is not a general reaction. The reaction of $[Co_3(CO)_9(CCO)]^+$ with PPh_3 leads to substitution at Co, yielding $[Co_3(CO)_8(PPh_3)(CCO)]^+$.[19] Thus the relative affinities of carbonyl and phosphine ligands for carbon and metal centers appear to be delicately balanced in these clusters.

The reaction shown in eq 1 is surprisingly facile considering the evidence for a strong C=CO bond in **1** (C–CO distance = 1.29 (5) Å[5] and $^1J_{CC}$ = 79.4 Hz[15]). The kinetic facility of this ligand displacement reaction at carbon may be the result of a transition state in which a ligand bridges between the metal framework and the capping carbon atom. A transition state of this type has been proposed in the synthesis of $H_2Ru_3(CO)_9(C\text{-}CO)$.[20] Evidence for incipient ligand bridging is evident in the structure of **1**, in which the CCO moiety tilts toward one Fe atom,[21] thus forming a semibridging CO between the C and Fe atoms. Ligand bridging may also facilitate the previously cited exchange of the carbon-bound CO ligand of **1** with gaseous ^{13}CO and to the displacement of the carbon-bound proton of **4** by PMe_3 (Scheme I). The tendency for the $M_3(CO)_9$ ensemble to delocalize electron density from the capping carbon atom may also lower the energy of the transition state for ligand exchange.

Acknowledgment. This research was supported by the NSF Synthetic Inorganic–Organometallic Chemistry Program.

Supplementary Material Available: Tables of crystal data, positional parameters, anisotropic thermal parameters, and bond distances and angles for $[PPN][Fe_2Co(CO)_9CP(CH_3)_3]$ (30 pages); tables of observed and calculated structure factors for $[PPN][Fe_2Co(CO)_9CP(CH_3)_3]$ (41 pages). Ordering information is given on any current masthead page.

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Photochemistry of Aryl Azides: Detection and Characterization of a Dehydroazepine by Time-Resolved Infrared Spectroscopy and Flash Photolysis at Room Temperature

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The photochemistry of the aromatic azides (ArN_3) has been a subject of interest and some controversy for more that 60 years.[3] Their irradiation leads to loss of nitrogen and to the formation of one or more reactive intermediates. For example, irradiation of phenyl azide creates its excited singlet state which loses nitrogen to give the singlet nitrene. Singlet phenylnitrene can intersystem cross to form its ground-state triplet which has been detected by ESR spectroscopy.[4] Azobenzene is formed by dimerization of

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[1] University of Illinois.

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[3] *Azides and Nitrenes*; Scriven, E. F. V., Ed.; Academic Press: 1984; Chapters 3 and 7.

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