frared data. The CO substitution reaction cannot be extended to bulky phosphines, and the rate of the migration step is qualitatively related to phosphine basicity.

The effects of phosphine substitution on the structure and reactivity of the CCO ligand were examined in the case of $[Fe_2Co(CO)_7(dmpm)(CCO)]^-$. This cluster contains a ketenylidene ligand that is tilted toward one of the phosphine-substituted metal centers. The chemistry of $[Fe_2Co(CO)_7(dmpm)(CCO)]^-$, in comparison to $[Fe_2Co(CO)_9(CCO)]^-$, indicates that the dmpm ligand labilizes the CO ligands toward exchange with gaseous ^{13}CO and increases the susceptibility of the CCO ligand toward electrophilic attack.

Phosphine migrations have recently become more prevalent in organometallic chemistry, and fluxional[36] and irreversible[8,17] processes are now known. But despite the ease with which $[Fe_2Co(CO)_9(CPR_3)]^-$ clusters are generated, ligand migration does not occur in all phosphine-substituted ketenylidene clusters as noted by the stability of $[Co_3(CO)_8(PPh_3)(CCO)]^+$.[20] Thus the relative affinities of carbonyl and phosphine ligands for a capping carbon atom appear to be delicately balanced. The propensity for phosphines to undergo migration in the $[Fe_2Co(CO)_8(PR_3)(CCO)]^-$ clusters may be related to the unique ability of anionic ketenylidene clusters to exchange the CO group of the CCO ligand with free CO.[3–6] This in turn may be related to the charge on the cluster.

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

Registry No. **1**, 88657-64-1; **2a**, 119145-53-8; **2b**, 119145-55-0; **2c**, 119145-57-2; **2d**, 119145-59-4; **2e**, 119145-61-8; **2f**, 119145-63-0; **3a**, 109284-18-6; **3b**, 119145-65-2; **3c**, 119145-67-4; **3d**, 119145-69-6; **3e**, 119145-71-0; **4**, 109284-19-7; **5**, 119145-72-1; **6**, 119145-74-3; **6**$\cdot CH_2Cl_2$, 119239-74-6; **7**, 119145-75-4; **8**, 119145-76-5; **9**, 119145-77-6; dmpm, 64065-08-3; ^{59}Co, 7440-48-4; PMe_3, 594-09-2; PMe_2Ph, 672-66-2; $PMePh_2$, 1486-28-8; PEt_3, 554-70-1; $P(OMe)_3$, 121-45-9; PPh_3, 603-35-0; PCy_3, 2622-14-2; HSO_3CF_3, 1493-13-6; $Co_2(CO)_8$, 10210-68-1; $Co_4(CO)_{12}$, 17786-31-1.

Supplementary Material Available: Tables of anisotropic thermal parameters, positional parameters not listed in the text, and bond distances and angles not listed in the text, and a packing diagram of the unit cell of $[PPN][Fe_2Co(CO)_7(dmpm)(CCO)]\cdot CH_2Cl_2$ (10 pages); a listing of observed and calculated structure factors (37 pages). Ordering information is given on any current masthead page.

A Diphosphine Ligand as a Bridge between Carbide and Metal Centers in Clusters

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The reaction of $[PPN][Fe_2Co(CO)_9(CCO)]$ with dmpe (dmpe = 1,2-bis(dimethylphosphino)ethane) generates an ylide-capped cluster, $[PPN][Fe_2Co(C)(dmpe)(CO)_8]$ (**1**), in which dmpe bridges the carbide ligand and cobalt atom. Protonation of **1** occurs across the Fe–Fe bond to give $HFe_2Co(C)(dmpe)(CO)_8$ (**2**), which retains the ylide moiety but has the phosphine bonded to an Fe center on the metal framework instead of the Co atom. Treatment of **1** with $Co_2(CO)_8$ leads to the isolation of $FeCo_2(CO)_9(\mu_3\text{-}CPMe_2CH_2CH_2Me_2PFe(CO)_4)$ (**3**), in which dmpe bridges between the cluster and a mononuclear species. Clusters **1**–**3** are all spectroscopically characterized. The molecular structure of **3** has been determined by single-crystal X-ray diffraction. Compound **3** crystallizes in the space group $P1$ with a = 9.392 (1) Å, b = 10.847 (2) Å, c = 7.946 (1) Å, α = 107.76 (1)°, β = 110.56 (1)°, γ = 88.73 (1)°, V = 718.5 (4) Å^3, and Z = 1.

Introduction

Our current research on the reactivity of $[Fe_2Co(CO)_9(CCO)]^-$ with phosphine ligands was prompted by the discovery of an unusual substitution–isomerization sequence which ultimately generates a capping ylide moiety from a capping ketenylidene ligand.[1,2] In the course of these studies we have synthesized a new ylide-containing cluster, $[Fe_2Co(C)(dmpe)(CO)_8]^-$ (dmpe = 1,2-bis(dimethylphosphino)ethane), in which the diphosphine ligand chelates across a metal–carbon bond. We thought that this type of chelation might stabilize the ylide moiety in cluster-building reactions. We discovered previously that the reaction of $[Fe_2Co(CO)_9(CPMe_3)]^-$ with $Co_2(CO)_8$ results in degradation of the ylide group and produces a carbide-containing cluster, $Fe_2Co_2(C)(CO)_{11}(PMe_3)$, along with significant quantities of $Co_4(CO)_{12}$.[2] In this paper, we report the synthesis of $[PPN][Fe_2Co(C)(dmpe)(CO)_8]$ and its reactivity with acid and $Co_2(CO)_8$.

Experimental Section

General Procedures and Materials. All manipulations were performed under a purified N_2 atmosphere by using standard Schlenk and syringe techniques[3] or in a Vacuum Atmospheres drybox unless noted otherwise. Solvents were distilled from appropriate drying agents and deaerated with N_2 before use.[4] Dmpe (Strem) was used as received (dmpe = 1,2-bis(dimethylphosphino)ethane). HSO_3CF_3 (Aldrich) was distilled before use.

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[2] Ching, S.; Sabat, M.; Shriver, D. F., *Organometallics*, preceding paper in this issue.

[3] Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley: New York, 1986.

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$Co_2(CO)_8$ (Strem) was freshly sublimed before use. $[PPN][Fe_2Co(CO)_9(CCO)]$ was prepared by a published procedure[5] (PPN = bis(triphenylphosphine)nitrogen(1+)). Spectroscopic methods and instrumentation were described in the previous paper.[2]

$[PPN][Fe_2Co(C)(dmpe)(CO)_8]\cdot Me_2CO$ (1·Me_2CO). A 1.00-g (1.00-mmol) sample of $[PPN][Fe_2Co(CO)_9(CCO)]$ was dissolved in 8 mL of CH_2Cl_2 and treated with 0.20 mL (1.2 mmol) of dmpe. After 4 h of stirring, the solution became green-black and the solvent was removed under vacuum. The resulting oil was dissolved in 12 mL of acetone and filtered. Addition of 40 mL of Et_2O followed by agitation of the flask produced black-purple crystals. The solution was cooled at 0 °C overnight and then further cooled at −78 °C for 3 h. The product was isolated by filtration, washed thoroughly with two 10-mL portions of MeOH, washed with Et_2O, and dried under vacuum. Yield: 0.84 g (73%). IR: (CH_2Cl_2) ν_{CO} 1992 (m), 1928 (s), 1902 (m), 1877 (w, sh), 1862 (w, sh), 1843 (vw, sh) 1710 (Me_2CO) cm^{-1}. ^1H NMR (CD_2Cl_2, +25 °C): 2.17 (m, 2 H, CH_2), 2.08 (s, 6 H, Me_2CO), 1.77 (d, 6 H, $^2J_{PH}$ = 11.6 Hz, $P(CH_3)_2$), 1.72 (m, partially obscured by 1.77 ppm resonance, 2 H, CH_2), 1.37 (d, 6 H, $^2J_{PH}$ = 7.2 Hz, $P(CH_3)_2$) ppm. ^{31}P NMR (CD_2Cl_2, −90 °C) second-order: 25.9 (d, $J_{PP}(AB)$ = 29.3 Hz, C–P), 19.6 (br, Co–P) ppm. ^{13}C NMR (1:2 $CD_2Cl_2/CHFCl_2$): −120 °C, 222.9 (6 CO, $Fe(CO)_3$), 215.9 (2 CO, $Co(CO)_2$), 188.6 (d, $^1J_{PC}$ = 33.0 Hz, μ_3-C) ppm; −90 °C, 220.7 (CO), 186.1 (d, $^1J_{PC}$ = 33.0 Hz, μ_3-C) ppm. Anal. Calcd for $C_{54}H_{52}CoFe_2NO_9P_4$: C, 56.24; H, 4.51; P, 9.69; Co, 5.11; Fe, 10.75. Found: C, 56.00; H, 4.68; P, 10.26; Co, 5.45; Fe, 11.36.

$HFe_2Co(C)(dmpe)(CO)_8$ (2). A 0.20-g (0.17-mmol) sample of $[PPN][Fe_2Co(C)(dmpe)(CO)_8]\cdot Me_2CO$ was dissolved in 6 mL of CH_2Cl_2, and 18 μL (0.20 mmol) of HSO_3CF_3 was added with stirring. An immediate color change to orange-brown was observed, and after 5 min the solvent was removed under vacuum. The resulting oil was extracted with 10 mL of Et_2O and filtered to remove $[PPN][SO_3CF_3]$. The Et_2O was removed under vacuum, and the oil was redissolved in 4 mL of CH_2Cl_2. This solution was passed down a column of Florisil (ca. 6 cm long with 1 cm diameter) under a N_2 purge and eluted with CH_2Cl_2. A single purple-brown band was collected, and the solvent was removed under vacuum. The product was redissolved in 2 mL of CH_2Cl_2 and layered with 10 mL of pentane. Cooling overnight at 0 °C produced black-purple crystals that were isolated by filtration, washed with pentane, and vacuum dried. Yield: 0.06 g (62%). IR: (CH_2Cl_2) ν_{CO} 2047 (m), 1993 (m, sh), 1978 (s), 1931 (w) cm^{-1}. MS: parent ion m/e 558 with successive loss of eight CO units. ^1H NMR (CD_2Cl_2, +25 °C): 2.42 (m, 2 H, CH_2), 2.04 (d, overlapping with 2.03 peak, 3 H, $^2J_{PH}$ = 12.7 Hz, CH_3), 2.03 (d, overlapping with 2.04 peak, 3 H, $^2J_{PH}$ = 11.7 Hz, CH_3), 2.00 (m, partially obscured, 2 H, CH_2), 1.60 (d, 3 H, $^2J_{PH}$ = 8.8 Hz, CH_3), 1.37 (d, 3 H, $^2J_{PH}$ = 8.8 Hz, CH_3), −19.28 (s, 1 H, HFe_2Co) ppm. ^{31}P NMR (CD_2Cl_2, −90 °C) second-order: 43.9 (d, C–P), 33.1 (d, Fe–P) ppm, $J_{PP}(AB)$ = 22.6 Hz. ^{13}C NMR (CD_2Cl_2, −90 °C): 214.9 (s, 3 CO, $Co(CO)_3$), 214.5 (d, 1 CO, $^2J_{PC}$ = 13.1 Hz, $Fe(CO)_2P$), 213.9 (s, 1 CO, $Fe(CO)_3$), 212.8 (d, 1 CO, $^2J_{PC}$ = 25.3 Hz, $Fe(CO)_2P$), 211.6 (s, 1 CO, $Fe(CO)_3$), 207.9 (s, 1 CO, $Fe(CO)_3$), 182.8 (d, $^1J_{PC}$ = 23.9 Hz, μ_3-C) ppm. Anal. Calcd for $C_{15}H_{17}CoFe_2O_8P_2$: C, 32.30; H, 3.05. Found: C, 31.70; H, 2.90.

$FeCo_2(CO)_9(\mu_3\text{-}CPMe_2CH_2CH_2Me_2PFe(CO)_4)$ (3). A 0.10-g (0.087-mmol) sample of $[PPN][Fe_2Co(C)(dmpe)(CO)_8]\cdot Me_2CO$ and 0.04 g (0.1 mmol) of $Co_2(CO)_8$ were dissolved in 6 mL of CH_2Cl_2 and stirred for 30 min to give a brown solution. The solvent was removed under vacuum, and the resulting oil was extracted in 8 mL of Et_2O and then filtered to remove $[PPN][Co(CO)_4]$. The solvent was removed under vacuum, and the oily solid was dissolved in 1 mL of CH_2Cl_2. Pentane (2 mL) was added before the solution was layered with 3 mL of pentane. Cooling at 0 °C overnight produced black-purple crystals and oil. Pure crystals were obtained by filtration, followed by two washings with 5 mL of MeOH and one washing with pentane. The product was dried under vacuum. Yield: 0.02 g (30%). IR: (CH_2Cl_2) ν_{CO} 2077 (w), 2052 (w), 2028 (s), 2012 (vs), 1978 (w), 1939 (m), 1930 (m, sh) cm^{-1}. MS: parent ion m/e 756, next peak at m/e 672 with successive loss of 10 CO units and one C_2H_4 unit. ^1H NMR (CD_2Cl_2, +25 °C): 2.45 (m, 2 H, CH_2), 2.17 (m, 2 H, CH_2), 1.97 (d, 6 H, $^2J_{PH}$ = 12.0 Hz, $P(CH_3)_2$), 1.69 (d, 6 H, $^2J_{PH}$ = 9.8 Hz, $P(CH_3)_2$) ppm. ^{31}P NMR (CD_2Cl_2, −90 °C) second-order: 50.5 (d), 41.0 (d) ppm, $J_{PP}(AB)$ = 42.2 Hz. ^{13}C NMR (CD_2Cl_2, −90 °C): 213.3 (d, 4 CO, $^2J_{PC}$ = 20.0 Hz, $Fe(CO)_4$), 210.8 (d, $^1J_{PC}$ = 26.8 Hz, μ_3-C), 206.2 (s, 9 CO, $FeCo_2(CO)_9$) ppm. Anal. Calcd for $C_{20}H_{16}Co_2Fe_2O_{13}P_2$: C, 31.78; H, 2.12; Fe, 14.78; Co, 15.60. Found: C, 32.10; H, 2.11; Fe, 15.30; Co, 15.75.

Table I. Crystal Data for $FeCo_2(CO)_9(\mu_3\text{-}CPMe_2CH_2CH_2Me_2PFe(CO)_4)$ (3)

formula	$Co_2Fe_2P_2O_{13}C_{20}H_{16}$
M	755.85
crystal size, mm	0.20 × 0.30 × 0.38
crystal system	triclinic
space group	$P1$
a, Å	9.392 (1)
b, Å	10.847 (2)
c, Å	7.946 (1)
α, deg	107.76 (1)
β, deg	110.56 (1)
γ, deg	88.73 (1)
V, $Å^3$	718.5 (4)
Z	1
d(calcd), g cm^{-3}	1.75
d(exptl), g cm^{-3}	1.74
μ(Mo Kα), cm^{-1}	22.9
radiation	Mo Kα (λ = 0.71069 Å), monochromated
scan type	$\omega/2\theta$
2θ range, deg	4–55
unique data	2522
unique data, $I > 3\sigma(I)$	2469
no. of parameters	350
$R(F)$	0.018
$R_w(F)$	0.025
GOF	0.897

X-ray Crystal Structure of $FeCo_2(CO)_9(\mu_3\text{-}CPMe_2CH_2CH_2Me_2PFe(CO)_4)$ (3). Black-purple crystals of the cluster were grown by slow diffusion of pentane into a CH_2Cl_2 solution at 0 °C. A crystal of **3** suitable for X-ray analysis was mounted on a glass fiber in air and then transferred to the cold stream of N_2 gas (−120 °C) on an Enraf-Nonius CAD4 diffractometer (Mo Kα radiation). A summary of the data collection of **3** is given in Table I. Preliminary measurements suggested a triclinic unit cell. Cell reduction calculations using the program TRACER did not yield a cell of higher symmetry that would describe the lattice. The density of the crystal as measured by flotation in a $CCl_4/CHBr_3$ system indicated a single cluster molecule in the unit cell. This led to the assumption that the compound crystallizes in the acentric space group $P1$. The successful solution and refinement of the structure confirmed this choice. The unit cell parameters were determined by the application of least-squares refinement to the setting angles of 25 unique reflections. These were confirmed by use of the same method on a second crystal. The intensities of four standard reflections were measured every 3 h. No appreciable decrease in intensity was observed, so a correction for decay was not applied. The collected data were corrected for Lorentz and polarization effects. Empirical absorption corrections were applied based on ψ scans of six Bragg reflections. The transmission factors ranged from 0.695 to 1.000.

All calculations were done by using the TEXSAN 2.0 program package[6] run on a VAX 11/730 computer. The structure was determined by direct methods (SHELXS 86)[7] and difference Fourier techniques. Least-squares refinement was performed with isotropic thermal parameters initially and then with anisotropic parameters. All hydrogen atoms were located on a difference Fourier map and introduced into the calculations without refinement. The largest peak in the final difference map (0.269 e/$Å^3$) was located near the metal atom designated as Fe1. Inversion of all atomic coordinates followed by least-squares refinement gave an increased R value of 0.023. Exchanging Fe1 and Co1 also increases R to 0.023 (R_w = 0.031) and yields less favorable thermal

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(5) Ching, S.; Holt, E. M.; Kolis, J. W.; Shriver, D. F. *Organometallics* **1988**, *7*, 892.

(6) Swepston, P. N. TEXSAN, Version 2.0, the TEXRAY Structure Analysis Program Package, Molecular Structure Corporation, College Station, TX, 1986.

(7) Sheldrick, G. M. SHELXS-86, A program for crystal structure determination; University of Goettingen, FRG, 1986.

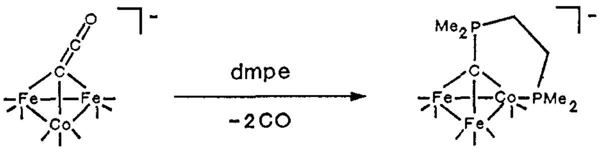
Table II. Positional Parameters for FeCo$_2$(CO)$_9$(μ_3-CPMe$_2$CH$_2$CH$_2$Me$_2$PFe(CO)$_4$) (3)

atom	*x*	*y*	*z*
Col	0.5622	0.1724	0.3205
Co2	0.66914 (6)	0.01493 (6)	0.10241 (7)
Fel	0.57101 (6)	−0.06135 (5)	0.31296 (7)
Fe2	−0.07970 (7)	−0.47477 (5)	−0.78184 (8)
P1	0.2887 (1)	−0.02495 (8)	−0.0518 (1)
P2	0.1252 (1)	−0.41242 (9)	−0.5164 (1)
O11	0.8525 (3)	−0.0463 (3)	0.6385 (4)
O12	0.3543 (4)	−0.0838 (3)	0.4908 (4)
O13	0.5097 (4)	−0.3398 (3)	0.1101 (4)
O21	0.6733 (4)	−0.2419 (3)	−0.1568 (5)
O22	0.6544 (4)	0.1689 (3)	−0.1485 (4)
O23	0.9886 (3)	0.0576 (5)	0.3675 (5)
O31	0.4823 (4)	0.3688 (3)	0.1242 (4)
O32	0.8548 (4)	0.2791 (4)	0.6367 (4)
O33	0.3533 (4)	0.2295 (3)	0.5283 (4)
O41	−0.2600 (4)	−0.4121 (4)	−0.5351 (5)
O42	0.0319 (5)	−0.7309 (3)	−0.8718 (6)
O43	−0.3499 (4)	−0.5453 (3)	−1.1342 (4)
O44	0.0348 (6)	−0.2894 (5)	−0.9130 (7)
C1	0.4714 (3)	0.0129 (3)	0.1212 (4)
C2	0.2372 (4)	0.0862 (3)	−0.1873 (5)
C3	0.1464 (4)	−0.0234 (3)	0.0512 (5)
C4	0.2801 (4)	−0.1885 (3)	−0.2085 (5)
C5	0.1313 (4)	−0.2407 (3)	−0.3776 (5)
C6	0.3069 (5)	−0.4283 (4)	−0.5517 (7)
C7	0.1408 (5)	−0.4998 (4)	−0.3491 (6)
C11	0.7451 (4)	−0.0531 (4)	0.5112 (5)
C12	0.4407 (4)	−0.0716 (3)	0.4225 (5)
C13	0.5400 (4)	−0.2315 (4)	0.1908 (5)
C21	0.6709 (4)	−0.1430 (4)	−0.0563 (6)
C22	0.6615 (4)	0.1103 (3)	−0.0491 (5)
C23	0.8643 (4)	0.0408 (5)	0.2628 (5)
C31	0.5156 (4)	0.2932 (3)	0.2008 (5)
C32	0.7421 (4)	0.2388 (4)	0.5158 (5)
C33	0.4345 (4)	0.2061 (3)	0.4484 (5)
C41	−0.1916 (5)	−0.4359 (4)	−0.6321 (6)
C42	−0.0134 (5)	−0.6325 (4)	−0.8362 (6)
C43	−0.2468 (5)	−0.5186 (3)	−0.9956 (5)
C44	−0.0107 (6)	−0.3594 (4)	−0.8599 (7)

parameters. The final positional parameters are listed in Table II.

Results and Discussion

Synthesis and Characterization of [PPN][Fe$_2$Co(C)(dmpe)(CO)$_8$] (1). The reaction of [PPN][Fe$_2$Co(CO)$_9$(CCO)] with the bidentate phosphine ligand dmpe (dmpe = 1,2-bis(dimethylphosphino)ethane) results in the substitution of two carbonyl ligands to give the ylide-capped cluster [PPN][Fe$_2$Co(C)(dmpe)(CO)$_8$] (1) (eq 1).



(1)

1

The dmpe ligand in cluster 1 spans the cobalt–carbon bond. In contrast to the chemistry observed for monodentate phosphine ligands,[2] no intermediate phosphine-substituted clusters are detected during the reaction of [Fe$_2$Co(CO)$_9$(CCO)]$^-$ with dmpe. Thus if dmpe coordinates to the cluster in a two-step process, the second step must be very rapid. Cluster 1 crystallizes from acetone–Et$_2$O with an acetone molecule of crystallization that was detected by IR and ^{1}H NMR spectroscopies.

The strongest band in the infrared spectrum of 1 occurs at 1928 cm^{-1}, which is very low for a mononegatively charged cluster. The strong IR bands of analogous clusters containing monodentate phosphine ligands are over 20 cm^{-1} higher,[2] indicating a high degree of electron donation from the phosphine ligand to the metal framework. A comparison of the IR spectrum of 1 with that of its metal-chelated analogue [Fe$_2$Co(CO)$_7$(dmpm)(CCO)]$^-$ (dmpm = bis(dimethylphosphino)methane),[2] which contains a main band at 1939 cm^{-1}, suggests that electron density is more effectively donated to the cluster when a phosphine coordinates to the capping carbon atom. This comparison supports a similar observation for the [Fe$_2$Co(CO)$_9$(CPR$_3$)]$^-$ and [Fe$_2$Co(CO)$_8$(PR$_3$)(CCO)]$^-$ clusters.[2]

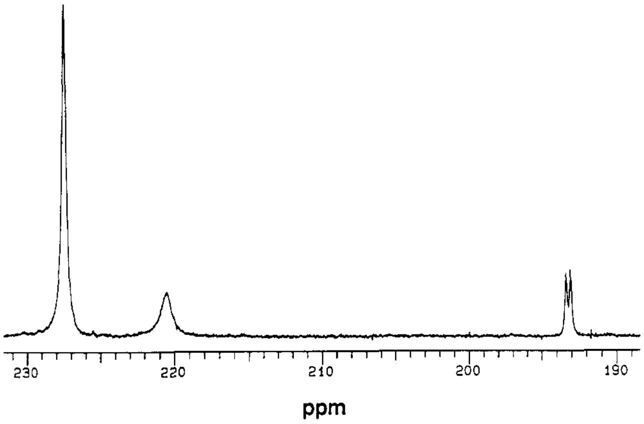
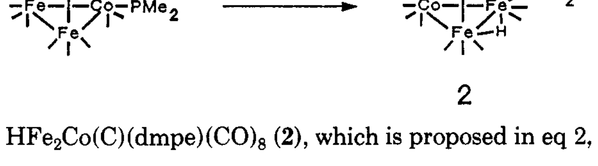


Figure 1. The ^{13}C NMR spectrum (100.577 MHz) of [PPN][Fe$_2$Co(C)(dmpe)(CO)$_8$] (1) recorded at −120 °C in 1:2 CD$_2$Cl$_2$/CHFCl$_2$.

The ^{1}H NMR spectrum of 1 exhibits resonances for two pairs of equivalent methyl groups and two pairs of equivalent methylene protons. The ^{31}P NMR spectrum recorded at −90 °C contains two resonances exhibiting second-order behavior. One of these broadens with increasing temperature, which is indicative of phosphine coordination to the Co atom. The ^{13}C NMR spectrum of 1 recorded at −90 °C exhibits a doublet characteristic of the capping carbon atom at 186.1 ppm while the carbonyl ligands are represented by a single resonance at 220.7 ppm. At −120 °C, the carbonyl resonance splits into a 3:1 pattern as CO exchange around the metal framework becomes slow on the NMR time scale (Figure 1). On the basis of the disposition of the CO ligands in the starting material, [Fe$_2$Co(CO)$_9$(CCO)]$^-$, the static structure of 1 is believed to possess C_1 symmetry, with the phosphorus atom coordinated to the Co metal center in an equatorial position (eq 1).[5] However, the NMR results presented above suggest that 1 has C_s symmetry in solution. This discrepancy may be reconciled by invoking a low-energy fluxional process in which the metal-coordinated end of the dmpe ligand oscillates rapidly between the two equatorial sites on the Co atom. Previous NMR studies of [Fe$_2$Co(CO)$_8$(PR$_3$)(CCO)]$^-$ clusters indicate that the Co(CO)$_2$(PR$_3$) vertex undergoes rapid turnstile rotation even at −130 °C.[2]

Reactivity of 1 with H$^+$. Protonation of 1 occurs on the metal framework and induces a curious shift in the coordination of the metal-bound phosphorus atom from the Co to Fe metal center (eq 2). The structure of HFe$_2$Co(C)(dmpe)(CO)$_8$ (2), which is proposed in eq 2, was



(2)

2

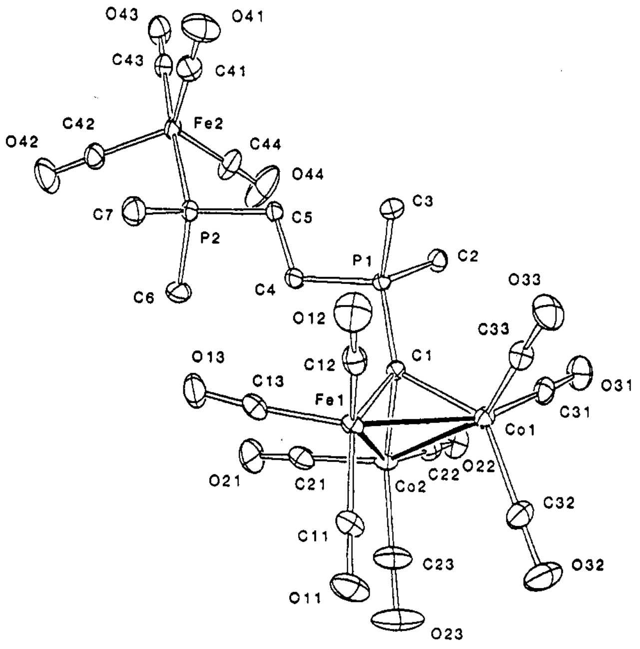
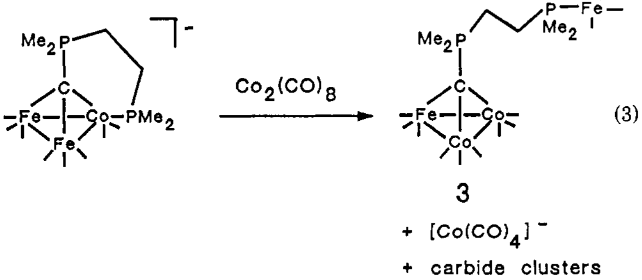


Figure 2. An ORTEP drawing of $FeCo_2(CO)_9(\mu_3\text{-}CPMe_2CH_2CH_2Me_2PFe(CO)_4)$ (3) showing 35% probability thermal ellipsoids.

deduced from the low-temperature ^{13}C NMR spectra. The hydride bridge across the Fe–Fe bond in 2 results in nonfluxional CO ligands at these metal vertices on the NMR time scale at −90 °C. Thus two doublets (214.5 and 212.8 ppm) can be assigned to the CO ligands on the phosphine-substituted Fe atom, and three singlet resonances (213.9, 211.6, and 207.9 ppm) can be assigned to the $Fe(CO)_3$ vertex. One resonance at 214.9 ppm is observed for the $Co(CO)_3$ vertex at −90 °C, indicating that the CO ligands are undergoing rapid turnstile rotation. At −60 °C this resonance is not observed because of line broadening caused by the quadrupolar ^{59}Co nucleus.

Reactivity of 1 with $Co_2(CO)_8$. The reaction of $[Fe_2Co(CO)_9(CPMe_3)]^-$ with $Co_2(CO)_8$ produces a four-metal butterfly carbide cluster as well as decomposition products.[2] A similar cluster-building reaction was attempted between 1 and $Co_2(CO)_8$ in order to determine whether or not the chelating dmpe ligand would (1) stabilize the cluster framework, thus inhibiting decomposition, and (2) stabilize the ylide moiety so that a higher nuclearity ylide-containing cluster might be formed preferentially over a carbide-containing cluster.

Treatment of 1 with $Co_2(CO)_8$ leads to the isolation of a completely unexpected product (eq 3). Instead of a



butterfly or a tetrahedral cluster, $FeCo_2(CO)_9(\mu_3\text{-}CPMe_2CH_2CH_2Me_2PFe(CO)_4)$ (3), was obtained in low yield (30%). This compound could not be formulated on the basis of spectroscopic data alone. Therefore, the molecular structure of 3 was determined by single-crystal X-ray diffraction. The molecular structure of 3 is displayed in Figure 2. The structure shows a $FeCo_2(CO)_9(\mu_3\text{-}C)$ cluster fragment and a mononuclear $Fe(CO)_4$ fragment linked by dmpe. Elemental analysis of 3 is consistent with a 1:1 ratio of Fe and Co atoms in the molecule. The positions assigned to Fe and Co in the structure were chosen on the assumption that the metal atoms would have a preference for 18 valence electrons at the $M(CO)_4$ site and 48 valence electrons at the $M_3(CO)_9$ site. The geometry of the cluster portion in 3 is similar to that of $[PPN][Fe_2Co(CO)_9(CPMe_3)]$.[1,2] The $FeCo_2(CO)_9$ frame is capped almost symmetrically by C1, with the P1–alkyl bonds staggered in relation to the vertices of the metal triangle. The C1-P1 distance of 1.742 (3) Å in 3 is slightly longer than that in $[PPN][Fe_2Co(CO)_9(CPMe_3)]$ (1.715 (3) Å), while the metal-metal distances are slightly shorter (average 2.510 Å in 3 compared to 2.545 Å for $[PPN][Fe_2Co(CO)_9(CPMe_3)]$). The $Fe(CO)_4(\eta^1\text{-dmpe})$ moiety has trigonal-bipyramidal coordination with P2 occupying an axial site. This same coordination geometry has been determined for $Fe(CO)_4$(phosphine) compounds in both the solid state[8-10] and solution.[11,12] The Fe2–P2 distance in 3 (2.224 (1) Å) is shorter than Fe–P bonds of structurally characterized $Fe(CO)_4L$ compounds ($L = PPh_2H, PPh_3, PBu^t{}_3$ with corresponding Fe–P distances = 2.237 (2),[8] 2.244 (1),[9] and 2.364 (1) Å,[10] respectively). In this series of compounds, the length of the Fe–P bond appears to be influenced by the relative size of the phosphine ligand. Selected bond distances and angles of 3 are listed in Table III.

Table III. Selected Bond Distances (Å) and Angles (deg) for $FeCo_2(CO)_9(\mu_3\text{-}CPMe_2CH_2CH_2Me_2PFe(CO)_4)$ (3)

	Bond Distances		
Co1–Co2	2.5040 (6)	P1–C1	1.742 (3)
Co1–Fe1	2.5181 (7)	P1–C2	1.802 (3)
Fe1–Co2	2.5088 (6)	P1–C3	1.793 (3)
Co1–C1	1.917 (3)	P1–C4	1.815 (3)
Co2–C1	1.916 (3)	P2–C5	1.843 (3)
Fe1–C1	1.887 (3)	P2–C6	1.820 (4)
Fe2–P2	2.224 (1)	P2–C7	1.821 (4)
Fe2–C41	1.803 (5)	C4–C5	1.527 (4)
Fe2–C42	1.787 (4)	C41–O41	1.137 (6)
Fe2–C43	1.801 (4)	C42–O42	1.132 (5)
Fe2–C44	1.779 (4)	C43–O43	1.142 (5)
		C44–O44	1.128 (6)
	Bond Angles		
Fe1–Co1–Co2	59.94 (2)	C3–P1–C2	106.4 (2)
Co1–Fe1–Co2	59.75 (2)	C3–P1–C4	107.9 (2)
Co1–Co2–Fe1	60.31 (2)	C2–P1–C4	109.8 (2)
C1–Co1–Co2	49.18 (9)	C6–P2–C7	103.8 (2)
C1–Co1–Fe1	48.03 (9)	C6–P2–C5	105.6 (2)
C1–Co2–Co1	49.22 (9)	C7–P2–C5	103.9 (2)
C1–Co2–Fe1	48.22 (8)	C5–P2–Fe2	112.4 (1)
C1–Fe1–Co2	49.21 (9)	C6–P2–Fe2	114.7 (2)
C1–Fe1–Co1	49.06 (9)	C7–P2–Fe2	115.4 (1)
Fe1–C1–Co2	82.6 (1)	C44–Fe2–C42	116.2 (2)
Fe1–C1–Co1	82.9 (1)	C44–Fe2–C43	90.1 (2)
Co1–C1–Co2	81.6 (1)	C44–Fe2–C41	123.9 (2)
P1–C1–Fe1	130.3 (2)	C44–Fe2–P2	88.4 (1)
P1–C1–Co2	131.5 (2)	C42–Fe2–C43	93.4 (2)
P1–C1–Co1	129.7 (2)	C42–Fe2–C41	119.5 (2)
C1–P1–C2	113.7 (1)	C42–Fe2–P2	88.7 (1)
C1–P1–C3	111.2 (1)	C43–Fe2–C41	92.8 (2)
C1–P1–C4	107.6 (1)	C43–Fe2–P2	177.7 (1)
P1–C4–C5	116.9 (2)	C41–Fe2–P2	86.7 (1)
P2–C5–C4	114.2 (2)		

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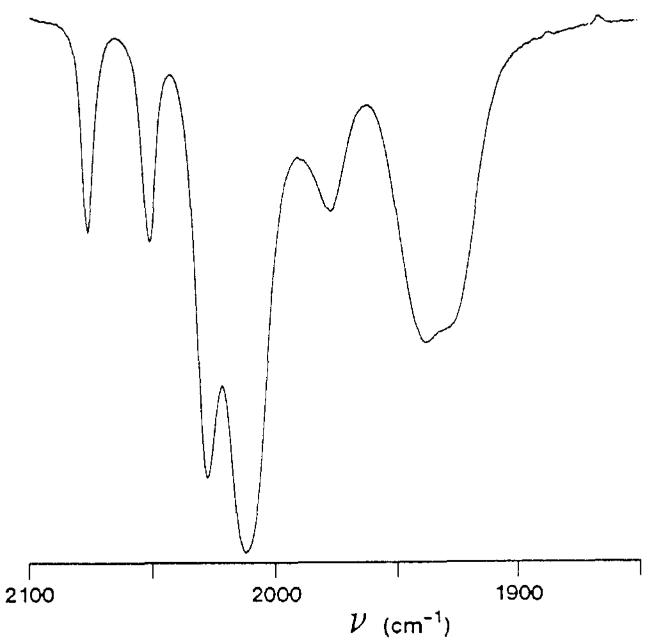

Figure 3. Infrared spectrum of 3 in CH_2Cl_2 solution.

The mass spectrum of **3** exhibits the expected parent ion at *m/e* 756. However, the next observed peak occurs at *m/e* 672 and the fragmentation pattern is consistent with either a butterfly or a tetrahedral cluster having the formula $Fe_2Co_2(C)(dmpe)(CO)_{10}$. The IR spectrum of **3** is shown in Figure 3. The lowest energy absorbances appear as a fairly intense band at 1939 cm^{-1} and a shoulder at 1930 cm^{-1}. These bands are in the region characterstic of absorbances due to the degenerate E modes of mononuclear $Fe(CO)_4(PR_3)$ compounds.[13,14] The observation of two bands in this region for **3** is believed to be due to splitting of the degenerate E modes in the $Fe(CO)_4$ portion of the molecule.[13] Alternatively, one band can be assigned to the $Fe(CO)_4$ group while the other band is assigned to the cluster portion of **3**. Similar assignments are also tentatively made for weaker bands at 1978 and 2052 cm^{-1}. These bands might represent the two A_1 modes of the $Fe(CO)_4$ group. The ^1H NMR spectrum of **3** is consistent with the presence of equivalent methyl groups on each phosphorus atom. The ^{31}P NMR spectrum at low temperature exhibits two doublets in a slightly second-order pattern. Neither resonance broadens significantly with increasing temperature, supporting the lack of a Co–P bond. The ^{13}C NMR spectrum of **3** recorded at −90 °C exhibits distinct resonances for the fluxional carbonyl ligands on the $FeCo_2(CO)_9$ and $Fe(CO)_4$ fragments. The resonance due to the capping carbon atom appears in the carbonyl region (210.8 ppm), and its assignment was confirmed by preparing a selectively enriched sample of **3**, $FeCo_2(^*CO)_9(\mu_3\text{-}CPMe_2CH_2CH_2Me_2PFe(^*CO)_4)$.[5]

Two other cluster compounds are detected from the reaction shown in eq 3. These were not isolated, but on the basis of their ^{13}C NMR resonances at 482.8 and 474.0 ppm, they are believed to be carbide-containing clusters.[15] The following integrated intensities are obtained from the ^{13}C NMR spectrum of the product mixture in eq 3: 3 (ylide):2 (474.0 ppm carbide):1 (482.8 ppm carbide). A trace amount of $Co_4(CO)_{12}$ was detected, but no $Fe(CO)_5$ or other decomposition products were observed. Since the production of **3** from **1** and $Co_2(CO)_8$ requires additional CO, the synthesis was performed under a CO atmosphere in an attempt to increase the yield of **3** and simultaneously suppress the formation of carbide clusters. However, the CO atmosphere suppresses all reactions of **1** with $Co_2(CO)_8$. When the CO atmosphere is replaced by N_2, the reaction follows its normal pathway. In comparison to the reaction of $[Fe_2Co(CO)_9(CPMe_3)]^-$ with $Co_2(CO)_8$,[2] the reaction in eq 3 proceeds with much less decomposition. However, even though the ylide moiety is retained to some extent in the formation of **3**, this product is a result of metal substitution rather than cluster building. Significant amounts of carbide-containing clusters are also generated.

The cluster portion of **3** contains a $Co(CO)_3$ group in place of $Fe(CO)_3$ in the starting material, and the displaced Fe fragment is trapped by one end of the dmpe ligand. Substitution of $Fe(CO)_3$ by $Co(CO)_3$ derived from $Co_2(CO)_8$ typically proceeds under mild conditions with the generation of $Fe(CO)_5$ as one of the side products.[5,16,17] However, in reaction 3 it appears that the formation of $Fe(CO)_5$ is intercepted by the metal-bound portion of the dmpe ligand so that a phosphine-substituted $Fe(CO)_4$ fragment is produced. Apparently, the $Fe(CO)_4(\eta^1\text{-dmpe})$ unit forms intramolecularly upon metal substitution. A bimolecular mechanism in which $FeCo_2(CO)_9(\mu_3\text{-}CPMe_2CH_2CH_2PMe_2)$ and $Fe(CO)_5$ form initially and then react seems unlikely since $Fe(CO)_5$ is substitutionally nonlabile at room temperature,[18] and the chelate effect with dmpe probably favors an intramolecular CO displacement on the cluster framework.

In related reactions, the $AsMe_2$ ligand has been shown to facilitate metal substitution by bridging between cluster and mononuclear fragments. The compounds $Co_3(\mu_3\text{-}CR)(CO)_8(\mu\text{-}AsMe_2)MCp(CO)_3$ (R = H, Me, Ph; M = Cr, Mo, W)[19] and $FeCo_2(\mu_3\text{-}S)(CO)_8(\mu\text{-}AsMe_2)MCp(CO)_3$ (M = Mo, W)[20],[21] contain an $AsMe_2$ bridge between M and a Co atom of the cluster. Upon heating, these clusters undergo metal substitution in which Cr, Mo, or W replace Co in the cluster portion of the molecule. Thermolysis of one of these compounds under vacuum results in aggregation of the metal fragments to give a tetrahedral, four-metal cluster.[21] A similar aggregation process seemed likely for **3** since volatilization of the compound during mass spectral analysis produces a prominent spectral feature corresponding to $[Fe_2Co_2(C)(dmpe)(CO)_{10}]^+$. However, when a solution of **3** is heated in DME for 4 h, no reaction occurs. Vacuum sublimation of **3** at 215 °C and 0.01 Torr results in extensive decomposition, and only a small amount of the starting material is recovered. The use of Me_3NO as a decarbonylating reagent[22] also did not lead to the formation of a tetranuclear cluster from **3**. Treatment of **3** with a 50-fold excess of Me_3NO results in slow decomposition of the cluster.

Conclusions

Even though dmpe bridges a carbide and metal center in $[Fe_2Co(C)(dmpe)(CO)_8]^-$, this ligand does not lead to the formation of higher nuclearity, ylide-capped clusters in the reaction of **1** with $Co_2(CO)_8$. Cluster building with

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$Co_2(CO)_8$ results in the formation of carbide-containing clusters. The ylide moiety is retained in a competing reaction as a bridge to a pendant metal atom. Similar instability toward cluster building is observed for CCO ligands in anionic clusters. Trimetallic ketenylidene-containing compounds are established precursors for higher nuclearity carbide clusters.[23] However, CCO ligands have not yet been reported for clusters with more than three metal atoms. The synthesis of $[PPN][Fe_2Co(CO)_9(CCO)]$ occurs by a metal substitution reaction which is similar to eq 3.[5]

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Registry No. 1, 119145-85-6; 2, 119145-86-7; 3, 119182-71-7; dmpe, 23936-60-9; $[PPN][Fe_2CO(CO)_9(CCO)]$, 88657-64-1; $Co_2(CO)_8$, 10210-68-1; CO, 7440-48-4; Fe, 7439-89-6.

Supplementary Material Available: Tables of anisotropic thermal parameters and bond distances and angles not cited in the text for 3 (3 pages); a listing of observed and calculated structure factors (17 pages). Ordering information is given on any current masthead page.

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Temperature Dependence of the Oxidative Addition of Triethylsilane to Photochemically Generated $(\eta^5\text{-}C_5Cl_5)Mn(CO)_2$

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Near-UV irradiation of $(\eta^5\text{-}C_5Cl_5)Mn(CO)_3$ in alkane glasses leads to the loss of CO to form a 16e dicarbonyl species. If the photolysis is effected in alkane solution containing Et_3SiH or in neat Et_3SiH, the dicarbonyl thermally reacts with the silane generating $(\eta^5\text{-}C_5Cl_5)Mn(CO)_2H(SiEt_3)$. The rate of the reaction is first order in $(\eta^5\text{-}C_5Cl_5)Mn(CO)_2$ and depends on temperature. The $\Delta H^{\ddagger}$ is 36 ± 4 kJ mol^{-1} and the $\Delta S^{\ddagger}$ is −140 ± 15 J mol^{-1} K^{-1} from rate measurements in the range 190–240 K. The significant finding is that the value of $\Delta H^{\ddagger}$ is about the same as that found for the reaction of Et_3SiH with photogenerated $(\eta^5\text{-}C_5H_5)Mn(CO)_2$ and $(\eta^5\text{-}C_5Me_5)Mn(CO)_2$. Thus, for the series $(\eta^5\text{-}C_5R_5)Mn(CO)_2$ (R = Cl, H, Me) variation in $\Delta S^{\ddagger}$, not $\Delta H^{\ddagger}$, is the source of the variation in the reaction rate with Et_3SiH. For R = Cl the reaction rate constant at a given temperature is extrapolated to be 10^7 times smaller than the reaction rate constant for R = Me.

We wish to report activation parameters for the oxidative addition of Et_3SiH to photogenerated $(\eta^5\text{-}C_5Cl_5)Mn(CO)_2$ (eq 1 and 2). A previous study on the oxidative addition of Et_3SiH to $(\eta^5\text{-}C_5R_5)Mn(CO)_3$ (R = H, Me) shows that $\Delta H^{\ddagger}$ values for the two complexes are the same and that the difference in the rate of reaction is governed by the difference in $\Delta S^{\ddagger}$.[1] Our new work concerns the oxidative addition to a Mn center with an electron-withdrawing cyclopentadienyl ring, C_5Cl_5.[2] Even though the rate for oxidative addition is found to be very slow compared to the $\eta^5\text{-}C_5H_5$ and $\eta^5\text{-}C_5Me_5$ species, we find $\Delta H^{\ddagger}$ to be nearly the same for all $\eta^5\text{-}C_5R_5$ complexes (R = Cl, H, Me).

$$(\eta^5\text{-}C_5Cl_5)Mn(CO)_3 \xrightarrow[-CO]{h\nu} (\eta^5\text{-}C_5Cl_5)Mn(CO)_2 \quad (1)$$

$$(\eta^5\text{-}C_5Cl_5)Mn(CO)_2 \xrightarrow{Et_3SiH} (\eta^5\text{-}C_5Cl_5)Mn(CO)_2H(SiEt_3) \quad (2)$$

The photochemistry of $(\eta^5\text{-}C_5Cl_5)Mn(CO)_3$ has not been detailed, but there is a considerable literature showing that $(\eta^5\text{-}C_5R_5)Mn(CO)_3$ complexes are photosensitive with respect to CO loss (eq 1).[1,3-7] Our new findings are in accord with CO loss as the only photoreaction of $(\eta^5\text{-}C_5Cl_5)Mn(CO)_3$. We have used low-temperature FTIR to quantitatively measure the rate of the thermal process represented by eq 2 under conditions where back reaction according to eq 3 is not competitive.

$$(\eta^5\text{-}C_5Cl_5)Mn(CO)_2 \xrightarrow{CO} (\eta^5\text{-}C_5Cl_5)Mn(CO)_3 \quad (3)$$

Experimental Section

Spectroscopy. IR spectra were recorded on a Nicolet 60SX or 170SX Fourier Transform spectrometer. Solutions of $(\eta^5\text{-}C_5Cl_5)Mn(CO)_3$ were contained in cells with CaF_2 windows. The low-temperature FTIR spectra were recorded with the cell mounted in a Specac Model P/N 21000 Dewar assembly, using a Neslab cryocool immersion cooler Model CC-100II and a Haake Model FS circulator. The temperature of the cell was monitored by using a Cu–constantan thermocouple in contact with the inner window of the cell. NMR spectra were recorded on a Varian

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