Cationic Vinylidene Complexes. Preparation and Structural Characterization of (η^5-Cyclopentadienyl)(2-methyl-4,5-bis(diphenylphosphino)-2-penten-3-yl)iron (II). A Base-Induced Interligand Reaction in a Vinylidene Complex

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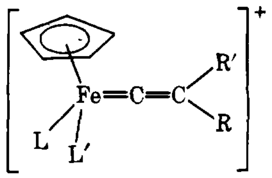
Abstract: The cationic vinylidene complex [(Cp)Fe(dppe){C═C(CH$_3$)$_2$}][SO$_3$F] (Ia) (dppe = 1,2-bis(diphenylphosphino)-ethane), prepared by the methylation of (Cp)Fe(dppe)(C≡CCH$_3$) (II), is smoothly deprotonated by potassium hydroxide or sodium bis(trimethylsilyl)amide. The exclusive product is (Cp)Fe[Ph$_2$PCH$_2$CH(PPh$_2$)C═C(CH$_3$)$_2$] (III), which contains a novel ferradiphospha[2.1.1]bicyclohexane ring system. This product was investigated by spectroscopic and crystal structure analysis: space group *Cc*, a = 14.738 (4) Å, b = 12.471 (5) Å, c = 16.982 (7) Å, β = 106.17 (3)°, V = 2997 (4) Å^3, Z = 4, ρ_{calcd} = 1.268 g/cm^3. Refinement on 1668 reflections with $F_o^2 > 3\sigma(F_o^2)$ has yielded the final discrepancy indices R = 0.058 and R_w = 0.060. The bicyclic ring system shows geometric and spectroscopic features which indicate that significant torsional strain is present. The formation of III has been explained by the intermediacy of a zwitterionic complex containing both a deprotonated dppe ligand ([Ph$_2$PCH$_2$CHPPh$_2$]) and a cationic vinylidene moiety. Subsequent intramolecular cyclization produces III.

Introduction

Little is known of the reaction chemistry of vinylidene complexes of transition metals (L$_n$M═C═CR$_2$).[1-7] Cationic vinylidene complexes have been observed to undergo addition of alcohols and water to product alkoxycarbene or acyl complexes,[1,2] displacement of and nucleophilic addition to the vinylidene ligand by hydride sources,[3b] and reversible deprotonation of monosubstituted vinylidene ligands at β-carbon atoms.[1,3a,4] Neutral vinylidene complexes have been observed to undergo thermal elimination of the vinylidene ligand,[5] interconversion of terminal and bridging vinylidene ligands,[6] and π coordination by an Fe(CO)$_3$ moiety.[7]

We have shown that electron-rich alkynyl complexes of iron readily react with electrophiles to produce stable cationic vinylidene complexes (Ia–d).[3] This reaction provides a convenient method for the preparation of such complexes, so that their chemistry can be systematically explored.



Ia, L + L′ = dppe;[8] R = R′ = CH$_3$
b, L + L′ = dppe; R = CH$_3$; R′ = H
c, L + L′ = dppe; R = R′ = H
d, L = L′ = P(CH$_3$)$_3$; R = R′ = CH$_3$

In this paper, we report the synthesis and characterization of the product obtained by the deprotonation of vinylidene complex Ia.

Experimental Section

General Procedures and Starting Materials. All operations involving the handling of organometallic complexes in solution were carried out under an atmosphere of prepurified nitrogen or argon. Air-sensitive materials were handled using standard inert atmosphere techniques, or in a Vacuum Atmospheres drybox. Ethers and hydrocarbon solvents were distilled from sodium benzophenone ketyl before use. Other solvents were degassed with a dispersed stream of dry nitrogen and stored over molecular sieves. Methyl fluorosulfonate (Aldrich) was distilled under nitrogen and stored at −15 °C. FeCl$_2$(thf)$_2$,[9] cyclopentadienylthallium (I),[10] and sodium bis(trimethylsilyl)amide[11] were prepared by literature methods. (Cp)Fe(dppe)Cl was prepared by a modification of the method of Mays and Sears.[12] Other reagents were used as received from commercial sources. ^{1}H NMR spectra were obtained on a Hitachi Perkin-Elmer R20B spectrometer (60 MHz) or a Bruker HFX270 spectrometer (270 MHz) and are reported in parts per million downfield from internal Me$_4$Si (δ). ^{13}C NMR spectra were obtained on a JEOL FX60Q spectrometer (15 MHz, FT mode) and are reported in parts per million downfield from internal Me$_4$Si (δ_C). ^{31}P NMR spectra were obtained on a Varian CFT 20 spectrometer (32.2 MHz, FT mode) and are reported in parts per million downfield from external aqueous H$_3$PO$_4$. Mass spectra were obtained at 70 eV on a Varian Associates MAT 44 (low resolution) or a Consolidated Electrodynamics Corp. 21-110 (high resolution). Infrared spectra were recorded on Perkin-Elmer Model 457A and 180 spectrophotometers. UV/visible spectra were obtained on a Cary Model 17 spectrophotometer. Melting points were determined on samples in sealed evacuated capillaries using a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, Tenn.

Preparation of (Cp)Fe(dppe)(C≡CCH$_3$). Propynyllithium (Alfa, 0.69 g, 15.0 mmol) and (Cp)Fe(dppe)Cl (5.0 g, 90.4 mmol) in 100 mL of THF were stirred for 7 h at room temperature. The solvent was removed in vacuo at 40–50 °C. The dark brown residue was extracted batchwise with benzene (ca. 50 mL) until the extracts were colorless, filtered, and reduced in volume. The red-brown solution was chromatographed on silica gel. Benzene eluted dark-colored impurities, and the product was eluted with ethyl ether. Recrystallization from warm benzene/heptane gave pure red-orange crystals (1.57 g, 32.3%, mp 178.5–180.5 °C).

Anal. Calcd for C$_{34}$H$_{32}$FeP$_2$: C, 73.13; H, 5.78; P, 11.09. Found: C, 73.02; H, 5.96; P, 10.90. Mass spectrum: parent ion *m/e* 558. IR: ν(C≡C) 2100 cm^{-1}. ^{1}H NMR (60 MHz, CDCl$_3$): δ 8.0–7.2 (20 H, Ph), 4.17 (t, $^3J_{PH}$ = 1.3 Hz, 5 H, Cp), 2.9–1.9 (m, 4 H, PCH$_2$), 1.60 (t, $^5J_{PH}$ = 2.15 Hz, 3 H, CH$_3$). ^{13}C NMR[13] (15 MHz, CDCl$_3$): 142.7–127.1 (m, Ph), 112.6 (s, C$_\alpha$), 97.5 (s, C$_\beta$), 78.8 (s, Cp), 28.4 (t, $^1J_{PC}$ = 22.5 Hz, PCH$_2$), 7.7 ppm (s, CH$_3$). UV/vis (CH$_3$CN): 475 nm, ϵ 450 (shoulder on intense UV absorption).

Preparation of [(Cp)Fe(dppe){C═C(CH$_3$)$_2$}]SO$_3$F. One gram (1.79 mmol) of (Cp)Fe(dppe)(C≡CCH$_3$) was dissolved in 25 mL of benzene, and 0.17 mL (0.24 g, 2.1 mmol) of methyl fluorosulfonate was added to the stirred solution during about 5 min. A pale orange solid precipitated on addition, and 15 mL of benzene was added to improve stirring. After 30 min the solids were filtered out, washed with benzene, ether, and petroleum ether, and dried in vacuo. The yield was

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quantitative (1.2 g). Recrystallization from $CHCl_3$ or CH_2Cl_2/benzene gave lustrous orange plates (mp 230.5–232.5 °C dec).

Anal. Calcd for $C_{35}H_{35}FFeO_3P_2S$: C, 62.51; H, 5.25; P, 9.21; S, 4.77. Found: C, 62.41; H, 5.30; P, 9.20; S, 4.45. IR: ν(C=C) 1675, $\nu(SO_3F^-)$ 1280, 1090, 1065 cm^{-1}. ^{1}H NMR (60 MHz, 1:1 $CDCl_3/CD_2Cl_2$): δ 7.7–6.9 (m, 20 H, Ph), 5.06 (t, $^3J_{PH} = 0.8$ Hz, 5 H, Cp), 2.86 (d, $^2J_{PH} = 13.0$ Hz, 4 H, PCH_2), 0.96 (t, $^5J_{PH} = 0.8$ Hz, 6 H, CH_3). ^{13}C NMR (1:1 $CDCl_3/CD_2Cl_2$): 363.3 (t, $^2J_{PC} = 33.3$ Hz, C_α), 136.5–129.6 (m, Ph), 127.8 (s, C_β), 88.0 (s, Cp), 28.4 (t, $^1J_{PC} = 23.0$ Hz, PCH_2), 12.0 ppm (s, CH_3).

Preparation of (Cp)$\overline{\text{Fe[Ph}_2\text{PCH}_2\text{CH(PPh}_2\text{)C}}$=C(CH$_3$)$_2$] (III). A. [(Cp)Fe(dppe){C=C(CH_3)$_2$}][SO_3F] (1.2 g, 1.8 mmol) was prepared from (Cp)Fe(dppe)(C≡CCH_3) (1.0 g) and CH_3SO_3F (0.17 mL) in benzene (50 mL). All volatiles were removed in vacuo and the pale orange solid was suspended in 30 mL of ethyl ether. Sodium bis(trimethylsilyl)amide (0.35 g, 1.9 mmol), was added over a period of about 1 min with vigorous stirring. After 5 min, the deep red solution was filtered and 5 mL of hexanes was added. The volume of the solution was reduced to 10 mL in vacuo, and it was cooled to −15°C overnight. Filtration, washing with petroleum ether, and drying in vacuo gave pure red crystals (0.67 g, 65.6%, mp 190–191 °C dec).

Anal. Calcd for $C_{35}H_{34}FeP_2$: C, 73.43; H, 5.99; P, 10.82. Found: C, 73.49; H, 6.10; P, 10.86. Mass spectrum: parent ion *m/e* 572.1442 (calcd, 572.1411); parent − PPh_2 *m/e* 387.0942 (calcd, 387.0965). IR (mulls): 1433 (s), 1094 (s, br), 850 (s), 799 (s), 751 (s), 742 (s), 715 (s), 697 (vs), 533 (s), 527 (s), 491 (s) cm^{-1}. ^{1}H NMR (270 MHz, C_6D_6): δ 7.82, 7.56, 7.39 (each has $J_{PH} \approx 8.0$, $J_{H-H} \approx 7.2$ Hz, 2 H, Ph_{ortho}), 7.2–6.9 (m, 14 H, Ph), 4.47 ($J_{P-Ha} = 44.8$, $J_{P'-Ha} = 7.3$, $^3J_{Ha-Hb} = 4.2$, $^3J_{Ha-Hc} \approx 0$ Hz, 1 H, $PCH_aCH_bH_cP$), 4.41 ($^3J_{PH} = 1.5$, $^3J_{P'H} = 0.7$ Hz, 5 H, Cp), 2.29 ($J_{P-Hb} = 43.3$, $J_{P'-Hb} = 10.1$, $^3J_{Ha-Hb} = 4.2$, $^2J_{Hb-Hc} = 13.0$ Hz, 1 H, $PCH_aCH_bH_cP$), 2.05 ($J_{PH} = 2.2$, $J_{P'-H} = 2.1$ Hz, 3 H, CH_3), 1.98 ($J_{PH} = 3.2$, $J_{P'H} = 3.0$ Hz, 3 H, CH_3), 1.87 ($J_{P-Hc} = 16.9$, $J_{P'-Hc} = 4.6$, $^3J_{Ha-Hc} \approx 0$, $^2J_{Hb-Hc} = 13.0$ Hz, 1 H, $PCH_aCH_bH_cP$). ^{13}C[^{1}H] NMR (15 MHz, C_6D_6): 147.9–126.3 (m, Ph + vinylic carbons), 74.4 (s, Cp), 56.9 (dd, $J_{PC} = 37.4$, $J_{P'-C} = 16.8$ Hz, CH), 33.3 (d, $J_{PC} = 35.2$ Hz, CH_2), 26.3 (d, $J_{PC} = 2.9$ Hz, CH_3), 20.9 ppm (poor t, $J_{PC} \approx J_{P'C} = 4.4$ Hz, CH_3). ^{31}P[^{1}H] NMR (32.2 MHz, C_6H_6): 86.63, 42.29 ppm (AB, $^3J_{P-P} = 44.8$ Hz).

B. In a septum-capped vial were placed [(Cp)Fe(dppe)-{C=C(CH_3)$_2$}][SO_3F] (ca. 50 mg) and potassium hydroxide (ca. 200 mg). THF (5 mL) and a few drops of water were added by syringe, and the slurry was shaken for 3 h at room temperature. The resulting orange-red solution was decanted from the oily aqueous layer, dried over $CaCl_2$, and reduced to dryness. The residual red oil was dissolved in 2 mL of ether and cooled to −15 °C overnight. The deep red crystals which formed were washed with pentane and dried in vacuo. Infrared and mass spectra identified the product as III.

Crystal Preparation and Data Collection for (CP)$\overline{\text{Fe[PPh}_2\text{CH}_2\text{CH(PPh}_2\text{)C}}$=C(CH$_3$)$_2$] (III). Single crystals were grown by recrystallization from ethyl ether at −20 °C. A thick, crystalline plate of approximate dimensions 0.09 × 0.20 × 0.35 mm was selected and mounted in a thin-walled glass capillary. The crystal faces were subsequently identified as 110, $\bar{1}$10, $\bar{1}$10, 1$\bar{1}$0, 00$\bar{1}$, and 001. The crystal was mounted with the c^* direction 13° from the diffractometer ϕ axis.

All diffraction measurements were performed using an Enraf-Nonius CAD-4 fully automated four-circle diffractometer using graphite monochromatized Mo Kα radiation. The unit cell was determined from 25 randomly chosen reflections using the CAD-4 search, center, index, and least-squares routines. Crystal data are listed in Table I.

From a total of 1880 reflections, 1668 conformed to the relation $F^2 \geq 3\sigma(F^2)$ and were used in the structure solution and refinement. The value of the p factor used in calculating $\sigma(F^2)$ was 0.02. Standard reflections monitored periodically showed less than 2% change in intensity during data collection. The linear absorption coefficient was 6.459 cm^{-1}, and no absorption correction was applied.

The pattern of systematic absences observed during data collection, *hkl*, $h + k = 2n + 1$, and *h*0*l*, $l = 2n + 1$, is consistent with either of the space groups $C2/c$ or Cc. The calculated density was 1.268 g/cm^3, indicating the presence of four molecules in the unit cell. Under these conditions the molecule would be required to contain a center of symmetry in space group $C2/c$. We considered this unlikely and thus chose the space group Cc to begin our calculations. The successful solution and refinement of the structure proved this choice to be correct.

Table I. Experimental Data for the X-ray Diffraction Study of (η^5-C_5H_5)$\overline{\text{Fe[PPh}_2\text{CH}_2\text{CH(PPh}_2\text{)C}}$=C(CH$_3$)$_2$]

A. Crystal Parameters at 23 °C	
space group	Cc
a	14.738 (4) Å
b	12.471 (5) Å
c	16.982 (7) Å
β	106.17 (3)°
V	2997 (4) Å^3
Z	4
mol wt	572.14
ρ_{calcd}	1.268 g cm^{-3}
B. Measurement of Intensity Data	
radiation	Mo Kα (0.710 73 Å)
monochromator	graphite
detector aperture	
horizontal: $A + B \tan\theta$	$A = 2.6$ mm $B = 1.2$ mm
vertical:	4 mm
reflections measured	$+h, +k, +l$
max 2θ	47°
scan type	moving crystal/stationary counter
scan width	0.8° + 0.347 tan θ
background	¼ additional scan at each end of scan
scan rate max	10°/min
min	1.3°/min
no. reflections measured	1880
data used ($F^2 > 3.0\ \sigma(F^2)$)	1668

All calculations were performed on a Digital PDP 11/45 computer using the Enraf-Nonius SDP program library. Anomalous dispersion corrections[14a] were included for the scattering[14b] of all nonhydrogen atoms. Least-squares refinements minimized the function $\Sigma_{hkl}w(F_o - F_c)^2$ where the weighting factor $w = 1/\sigma(F)^2$.

Solution and Refinement of the Structure. The positions of the iron and phosphorus atoms were determined from a Patterson map, and the positions of carbon atoms were obtained by successive difference Fourier techniques. Hydrogen atom positions were calculated and were included in structure factor calculations but they were not refined. Full-matrix least-squares refinement using anisotropic thermal parameters for the iron and phosphorus atoms and isotropic thermal parameters for the carbon atoms converged to the final residuals $R_1 = 0.058$ and $R_2 = 0.060$.

To test for the proper enantiomorph the signs of the coordinates of all atoms were reversed and three additional cycles of refinement were performed. The residuals were then $R_1 = 0.058$ and $R_2 = 0.061$. Although this difference is not significant, the final atomic coordinates and thermal parameters presented in Table II are based on the original model, since the value of R_2 for that model was slightly lower. The largest peaks in the final difference Fourier synthesis were 0.217 and 0.206 e/Å^3.

The largest value of the shift/error parameter on the final cycle of refinement was 0.05. The error in an observation of unit weight was 2.89. Bond distances and angles with errors from the inverse matrix obtained on the final cycle of least-squares refinement are listed in Tables III and IV. Tables of structure factors and intermolecular contacts are available (see supplementary material).

Results

Preparation of the Complex. The synthetic scheme shown below was used to prepare complex III. The reaction of (Cp)Fe(dppe)Cl[12] with LiC≡CCH_3 in THF gives (Cp)-Fe(dppe)(C≡CCH_3) (II) in 32% isolated yield. This product reacts rapidly and quantitatively with methyl fluorosulfonate in benzene to produce the isobutenylidene complex Ia. Deprotonation of Ia was accomplished with either aqueous potassium hydroxide in THF or sodium bis(trimethylsilyl)amide in ethyl ether. The latter reaction allows a simpler workup and yields analytically pure III in 66% yield. No products arising from nucleophilic attack at the vinylidene α carbon[3b] could be detected using either base.[15]

Table II. Final Positional and Thermal Parameters and Their Estimated Standard Deviations for $(Cp)Fe[PPh_2CH_2CH(PPh_2)C{=}C(CH_3)_2]$[a]

atom	*x*	*y*	*z*	*B*	atom	*x*	*y*	*z*	*B*
Fe	0.000	0.0262 (1)	0.0000		C(35)	−0.1292 (9)	−0.3919 (10)	−0.0059 (8)	5.6 (3)
P(1)	0.0749 (2)	−0.0303 (2)	0.1211 (2)		C(36)	−0.1186 (8)	−0.2853 (10)	0.0370 (7)	4.5 (3)
P(2)	−0.1207 (2)	−0.0596 (2)	0.0148 (2)		C(41)	−0.2394 (6)	−0.0059 (8)	−0.0327 (6)	3.0 (2)
C(11)	0.1014 (7)	−0.1681 (9)	0.1538 (6)	3.2 (2)	C(42)	−0.2495 (8)	0.0933 (10)	−0.0674 (7)	5.1 (3)
C(12)	0.0978 (8)	−0.2017 (9)	0.2308 (7)	4.3 (3)	C(43)	−0.3418 (10)	0.1377 (12)	−0.1049 (9)	6.7 (4)
C(13)	0.1145 (10)	−0.3095 (11)	0.2524 (9)	6.3 (3)	C(44)	−0.4173 (9)	0.0793 (11)	−0.1008 (8)	5.7 (3)
C(14)	0.1351 (9)	−0.3802 (11)	0.2024 (9)	6.4 (3)	C(45)	−0.4098 (8)	−0.0146 (10)	−0.0677 (7)	5.0 (3)
C(15)	0.1431 (10)	−0.3522 (12)	0.1274 (9)	6.5 (3)	C(46)	−0.3208 (8)	−0.0624 (9)	−0.0323 (7)	4.1 (2)
C(16)	0.1225 (9)	−0.2418 (10)	0.1024 (8)	5.1 (3)	C(51)	−0.1062 (7)	−0.0538 (8)	0.1281 (6)	3.3 (2)
C(21)	0.1824 (7)	0.0408 (8)	0.1765 (6)	3.4 (2)	C(52)	−0.0241 (7)	0.0210 (9)	0.1582 (6)	3.1 (2)
C(22)	0.2688 (8)	−0.0005 (9)	0.1789 (7)	4.3 (3)	C(61)	−0.0354 (7)	0.1142 (9)	0.0875 (6)	3.6 (2)
C(23)	0.3519 (8)	0.0531 (10)	0.2162 (8)	5.4 (3)	C(62)	−0.0608 (9)	0.2133 (11)	0.1063 (7)	5.4 (3)
C(24)	0.3524 (9)	0.1480 (10)	0.2532 (8)	5.6 (3)	C(63)	−0.0771 (10)	0.2455 (12)	0.1861 (9)	6.3 (3)
C(25)	0.2692 (11)	0.1930 (13)	0.2474 (10)	8.5 (5)	C(64)	−0.0705 (12)	0.2998 (15)	0.0469 (11)	9.5 (5)
C(26)	0.1827 (10)	0.1381 (13)	0.2157 (9)	7.3 (4)	CP(1)	0.0332 (9)	−0.0423 (10)	−0.1021 (8)	5.4 (3)
C(31)	−0.1379 (7)	−0.2004 (8)	−0.0171 (6)	3.2 (2)	CP(2)	−0.0364 (8)	0.0346 (11)	−0.1276 (8)	5.6 (3)
C(32)	−0.1679 (8)	−0.2235 (9)	−0.1001 (7)	3.9 (2)	CP(3)	−0.0054 (9)	0.1326 (11)	−0.0988 (8)	6.3 (3)
C(33)	−0.1756 (8)	−0.3297 (10)	−0.1268 (7)	4.8 (3)	CP(4)	0.0910 (9)	0.1185 (11)	−0.0497 (8)	5.8 (3)
C(34)	−0.1580 (9)	−0.4123 (11)	−0.0748 (8)	5.4 (3)	CP(5)	0.1110 (8)	0.0117 (10)	−0.0551 (8)	5.4 (3)

Anisotropic Thermal Parameters for the Iron and Phosphorus Atoms

	$\beta(1,1)$	$\beta(2,2)$	$\beta(3,3)$	$\beta(1,2)$	$\beta(1,3)$	$\beta(2,3)$
Fe	0.003 86 (6)	0.005 72 (9)	0.002 46 (4)	0.0005 (2)	0.002 17 (8)	0.0012 (2)
P(1)	0.0038 (1)	0.0045 (2)	0.002 45 (9)	0.0010 (3)	0.0014 (2)	−0.0011 (3)
P(2)	0.0035 (1)	0.0052 (2)	0.002 68 (10)	0.005 (3)	0.0018 (2)	0.0003 (3)

[a] The form of the anisotropic thermal parameter is $\exp[-(\beta(1,1)h^2 + \beta(2,2)k^2 + \beta(3,3)l^2 + \beta(1,2)hk + \beta(1,3)hl + \beta(2,3)kl)]$.

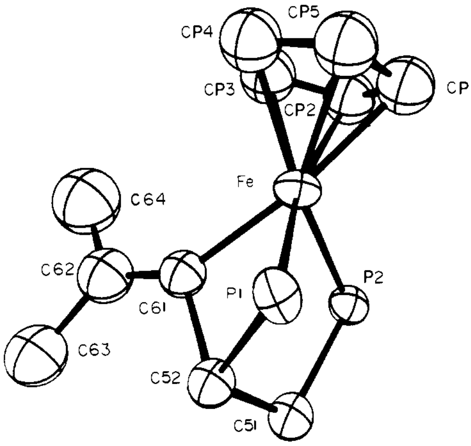


Figure 1. An ORTEP diagram of $(Cp)Fe[PPh_2CH_2CH(PPh_2)C{=}C(CH_3)_2]$ showing 50% probability ellipsoids. The phenyl groups have been eliminated for clarity.

$$CpFe(dppe)Cl + LiC{\equiv}CCH_3 \rightarrow (Cp)Fe(dppe)(C{\equiv}CCH_3)\ (II) \tag{1}$$

$$II + CH_3OSO_2F \rightarrow [(Cp)Fe(dppe)\{C{=}C(CH_3)_2\}][SO_3F]\ (Ia) \tag{2}$$

$$Ia + base \rightarrow III \tag{3}$$

Description of the Structure. The molecular structure of compound III is shown in Figures 1 and 2. Figure 1 emphasizes the central coordination sphere of the iron atom, which contains a symmetrically bonded *pentahapto*cyclopentadienyl ring, a vinylic carbon, and two phosphorus atoms. The most important feature of the structure is that the vinylic α carbon (C(61)) is bonded to both the iron atom and to one of the carbons in the ethylene bridge of the dppe ligand (C(52)). As a result, complex III contains a 1-ferra-2,5-diphospha-[2.1.1]bicyclohexane ring system. The torsional strain in the bicyclic ring system is reflected in its geometry. The four-membered ring has angles of 69.3 (2), 88.2 (2), 85.8 (4), and 99.0 (4)° at Fe, P(1), C(52), and C(61), respectively. This ring is "folded" with a dihedral angle of 47.4° between the Fe-P(1)-C(52) and the Fe-C(61)-C(52) planes. The C(61)-C(52) bond is abnormally long, 1.646 (9) Å. The Fe-C(61) bond length is 0.10 Å longer than the Fe-C (sp^2) bond in (Cp)Fe(dppe)C(O)Ph[16] (2.030 (7) Å). The five-membered rings show less sign of strain, although the P(2)-C(51)-C(52) angle is rather acute, 103.0 (4)°. The exocyclic double bond has a typical length for a carbon-carbon double bond, 1.36 (1)

Table III. Bond Distances with Errors for $(Cp)Fe[PPh_2CH_2CH(PPh_2)C{=}C(CH_3)_2]$

atoms	distance, Å	atoms	distance, Å
Fe-P(1)	2.164 (2)	C(16)-C(11)	1.363 (9)
Fe-P(2)	2.150 (2)	C(21)-C(22)	1.364 (9)
Fe-C(61)	2.030 (7)	C(22)-C(23)	1.385 (9)
Fe-CP(1)	2.110 (8)	C(23)-C(24)	1.339 (10)
Fe-CP(2)	2.084 (9)	C(24)-C(25)	1.327 (11)
Fe-CP(3)	2.123 (9)	C(25)-C(26)	1.415 (13)
Fe-CP(4)	2.114 (8)	C(26)-C(21)	1.384 (11)
Fe-CP(5)	2.107 (8)	C(31)-C(32)	1.385 (9)
P(1)-C(11)	1.815 (7)	C(32)-C(33)	1.394 (10)
P(1)-C(21)	1.830 (7)	C(33)-C(34)	1.335 (10)
P(1)-C(52)	1.856 (7)	C(34)-C(35)	1.340 (10)
P(2)-C(31)	1.834 (7)	C(35)-C(36)	1.424 (10)
P(2)-C(41)	1.837 (6)	C(36)-C(31)	1.378 (9)
P(2)-C(51)	1.877 (7)	C(41)-C(42)	1.360 (9)
CP(1)-CP(2)	1.383 (11)	C(42)-C(43)	1.441 (11)
CP(2)-CP(3)	1.349 (11)	C(43)-C(44)	1.348 (11)
CP(3)-CP(4)	1.444 (12)	C(44)-C(45)	1.290 (10)
CP(4)-CP(5)	1.373 (10)	C(45)-C(46)	1.414 (10)
CP(5)-CP(1)	1.377 (10)	C(46)-C(41)	1.392 (9)
C(11)-C(12)	1.388 (9)	C(51)-C(52)	1.500 (9)
C(12)-C(13)	1.397 (10)	C(52)-C(61)	1.646 (9)
C(13)-C(14)	1.316 (11)	C(61)-C(62)	1.355 (10)
C(14)-C(15)	1.357 (11)	C(62)-C(63)	1.496 (11)
C(15)-C(16)	1.448 (11)	C(62)-C(64)	1.455 (13)

Table IV. Bond Angles with Errors for (Cp)Fe[PPh$_2$CH$_2$CH(PPh$_2$)C=C(CH$_3$)$_2$]

atoms	angle, deg	atoms	angle, deg
P(1)-Fe-P(2)	86.96 (7)	C(21)-C(22)-C(23)	122.0 (7)
P(1)-Fe-C(61)	69.3 (2)	C(22)-C(23)-C(24)	122.0 (8)
P(2)-Fe-C(61)	78.1 (2)	C(23)-C(24)-C(25)	117.1 (9)
Fe-P(1)-C(11)	127.5 (2)	C(24)-C(25)-C(26)	122.6 (10)
Fe-P(1)-C(21)	118.1 (2)	C(25)-C(26)-C(21)	119.3 (9)
Fe-P(1)-C(52)	88.2 (2)	P(2)-C(31)-C(32)	118.6 (5)
C(11)-P(1)-C(21)	102.7 (3)	P(2)-C(31)-C(36)	123.5 (5)
C(11)-P(1)-C(52)	110.2 (3)	C(36)-C(31)-C(32)	117.8 (6)
C(21)-P(1)-C(52)	108.0 (3)	C(31)-C(32)-C(33)	120.2 (7)
Fe-P(2)-C(31)	119.5 (2)	C(32)-C(33)-C(34)	122.3 (8)
Fe-P(2)-C(41)	119.0 (2)	C(33)-C(34)-C(35)	118.6 (8)
Fe-P(2)-C(51)	103.8 (2)	C(34)-C(35)-C(36)	121.8 (8)
C(31)-P(2)-C(41)	100.6 (3)	C(35)-C(36)-C(31)	119.2 (7)
C(31)-P(2)-C(51)	107.9 (3)	P(2)-C(41)-C(42)	119.9 (5)
C(41)-P(2)-C(51)	105.0 (3)	P(2)-C(41)-C(46)	122.0 (5)
CP(5)-CP(1)-CP(2)	105.5 (8)	C(46)-C(41)-C(42)	118.2 (6)
CP(1)-CP(2)-CP(3)	111.6 (8)	C(41)-C(42)-C(43)	121.1 (8)
CP(2)-CP(3)-CP(4)	106.2 (8)	C(42)-C(43)-C(44)	117.4 (9)
CP(3)-CP(4)-CP(5)	106.0 (8)	C(43)-C(44)-C(45)	122.8 (9)
CP(4)-CP(5)-CP(1)	110.7 (8)	C(44)-C(45)-C(46)	121.6 (8)
P(1)-C(11)-C(12)	120.8 (5)	C(45)-C(46)-C(41)	118.9 (7)
P(1)-C(11)-C(16)	120.7 (6)	P(2)-C(51)-C(52)	103.0 (4)
C(16)-C(11)-C(12)	118.4 (7)	P(1)-C(52)-C(51)	107.8 (5)
C(11)-C(12)-C(13)	119.2 (7)	P(1)-C(52)-C(61)	85.8 (4)
C(12)-C(13)-C(14)	122.0 (9)	C(51)-C(52)-C(61)	106.4 (5)
C(13)-C(14)-C(15)	121.9 (9)	Fe-C(61)-C(52)	99.0 (4)
C(14)-C(15)-C(16)	117.0 (9)	Fe-C(61)-C(62)	144.1 (6)
C(15)-C(16)-C(11)	121.3 (8)	C(52)-C(61)-C(62)	116.9 (6)
P(1)-C(21)-C(22)	120.0 (5)	C(61)-C(62)-C(63)	125.6 (8)
P(1)-C(21)-C(26)	123.9 (6)	C(61)-C(62)-C(64)	119.6 (8)
C(26)-C(21)-C(22)	116.1 (7)	C(63)-C(62)-C(64)	114.8 (8)

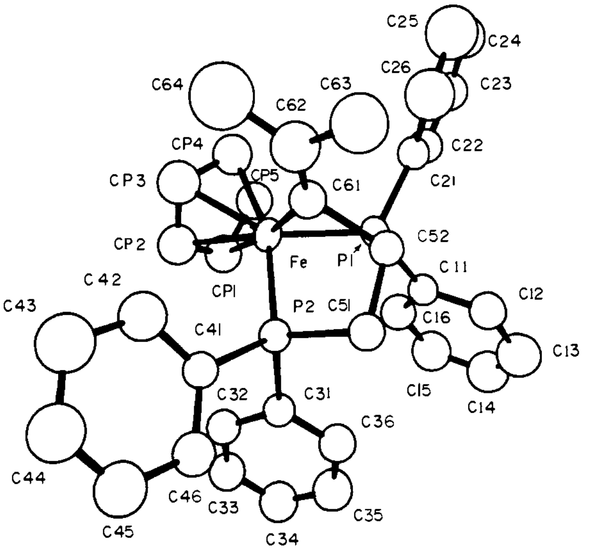


Figure 2. An ORTEP diagram of (Cp)Fe[PPh$_2$CH$_2$CH(PPh$_2$)C=C(CH$_3$)$_2$] showing 50% probability ellipsoids.

Å, and its substituents are nearly coplanar. The iron atom lies only 0.063 Å from the plane containing atoms C(61), C(62), C(63), C(64), and C(52). An Fe-C(61)-C(62) angle of 144.1 (6)° compensates for the very acute Fe-C(61)-C(52) angle. Other features of the coordination geometry of III are normal, and are in agreement with structural aspects of (Cp)Fe(dppe) complexes.[16,17]

The unit cell for III consists of four well-separated molecules with no unusually short intermolecular contacts between nonhydrogen atoms. The closest approach is between C(13) and C(32) of adjacent molecules, 3.50 Å apart.

Spectroscopic Characteristics of III. Typically, the mass spectra of CpFe(dppe)X complexes display moderately weak molecular ions and fragment ions arising from the loss of dppe.[3b,12c] The high-resolution mass spectrum of III, on the other hand, displays a fairly strong molecular ion and a fragment ion corresponding to the loss of a PPh$_2$ unit, reflecting the fact that the dppe ligand and the isobutenylidene moiety have become covalently linked.

The ^{31}P[^{1}H] NMR spectrum of III consists of an AB pattern for the two inequivalent phosphorus atoms, consistent with the lack of symmetry shown in its molecular structure. It is likely that P(2), which is contained in a five-membered chelate ring, is responsible for the downfield ^{31}P resonance (86.63 ppm), and that P(1), which is contained in a four-membered chelate ring, produces the higher field signal (42.29 ppm).[18]

^{1}H NMR spectra (270 MHz) of III show several interesting effects. The phenyl region exhibits remarkable fine structure, consisting of three well-separated apparent triplets each of relative intensity 2, at δ 7.82, 7.56, and 7.39, in addition to a complex multiplet from δ 7.2 to 6.9. The apparent triplets all have $J_{P-H} \approx 8.0$ Hz and collapse to doublets (with some fine structure) upon broad-band ^{31}P decoupling ($J_{H-H} \approx 7.2$ Hz). These resonances may be due to the ortho protons of the three phenyl rings which are held in close proximity to the sterically locked bicyclic ring system (Figure 2). The cyclopentadienyl group and the two methyl groups are all unequally coupled to the two phosphorus atoms. The remaining three protons (H$_a$ on C(52), H$_b$ and H$_c$ on C(51) of Figure 2) couple with the two phosphorus atoms to produce a very complex spin system (approximating ABMXY). By a combination of ^{31}P and selective ^{1}H decoupling, all proton shifts and coupling constants were determined (see Experimental Section). Of particular note is the strong downfield shift of H$_a$ on C(52), characteristic of a proton on the bridgehead carbon of a polycyclic system.[19] The bridgehead carbon resonance (C(52)) also occurs at low field[19] (δ_C 56.9 ppm) in the ^{13}C[^{1}H] NMR spectrum of III,

Table V. Various Unit Weighted Least-Squares Planes for $(CP)Fe[PPh_2CH_2CH(PPh_2)C{=}C(CH_3)_2]$[a]

plane no.	atoms	distance from plane
1	CP(1)	−0.003
	CP(2)	−0.003
	CP(3)	0.008
	CP(4)	−0.010
	CP(5)	0.008
	Fe*	−1.748
2	C(61)	−0.001
	C(62)	0.014
	C(63)	−0.003
	C(64)	−0.007
	C(52)	−0.003
	Fe*	−0.063
	P(1)*	−1.102
	P(2)*	1.764
3	C(11)	0.003
	C(12)	−0.012
	C(13)	0.005
	C(14)	0.012
	C(15)	−0.021
	C(16)	0.014
	P(1)*	0.059
4	C(21)	0.010
	C(22)	0.010
	C(23)	−0.001
	C(24)	−0.031
	C(25)	0.052
	C(26)	−0.041
	P1*	0.122
5	C(31)	0.003
	C(32)	−0.009
	C(33)	0.010
	C(34)	−0.006
	C(35)	0.000
	C(36)	0.001
	P(2)*	0.099
6	C(41)	0.002
	C(42)	−0.012
	C(43)	0.015
	C(44)	−0.007
	C(45)	−0.004
	C(46)	0.007
	P(2)*	−0.040

Dihedral Angles between Planes

planes	angle, deg
1-2	−75.9
2-4	88.5
2-6	78.0
3-4	87.2
3-5	−27.1
5-6	75.0

Equations of the Planes of the Form $AX + BY + CZ = D$

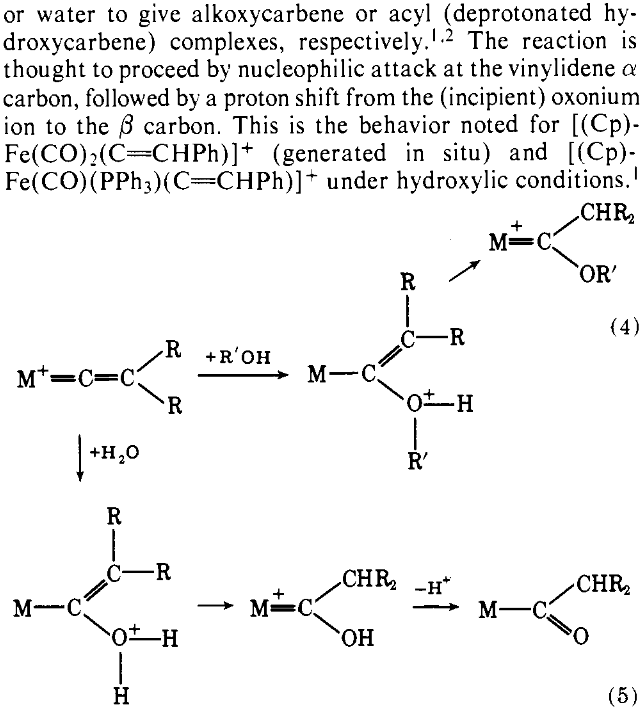
plane	A	B	C	D
1	0.5571	0.1749	−0.8118	1.8047
2	−0.9001	−0.2339	−0.3676	−0.0138
3	−0.9010	−0.2086	−0.3804	−1.2106
4	0.2095	0.4475	−0.8694	−1.8968
5	0.9996	0.0051	−0.0290	−1.9585
6	0.2354	−0.4166	−0.8781	−0.2967

[a] Atoms marked with an asterisk were not used in the calculation of the plane.

with $J_{PC} = 37.4$, $J_{P'C} = 16.8$ Hz. Other features of the ^{13}C NMR spectrum of III are normal. Resonances due to the olefinic carbons (C(61) and C(62)) were not found, presumably owing to long relaxation times and overlap with the intense phenyl multiplet.

Discussion

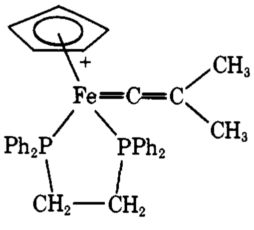
Most cationic vinylidene complexes (and "metal stabilized vinylcarbonium ions"[2]) react characteristically with alcohols or water to give alkoxycarbene or acyl (deprotonated hydroxycarbene) complexes, respectively.[1,2] The reaction is thought to proceed by nucleophilic attack at the vinylidene α carbon, followed by a proton shift from the (incipient) oxonium ion to the β carbon. This is the behavior noted for $[(Cp)Fe(CO)_2(C{=}CHPh)]^+$ (generated in situ) and $[(Cp)Fe(CO)(PPh_3)(C{=}CHPh)]^+$ under hydroxylic conditions.[1]



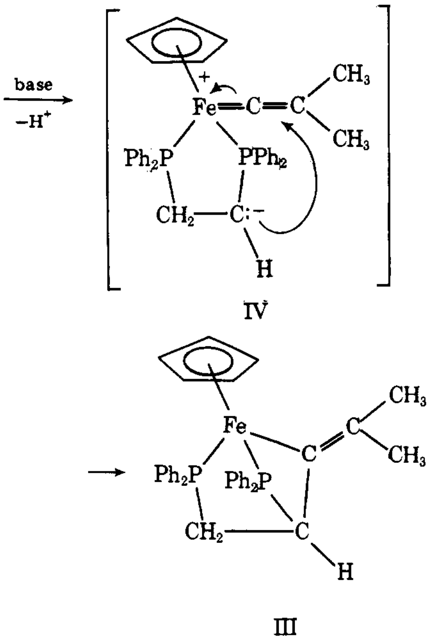
(4)

(5)

However, the bis(phosphine) substituted vinylidene complexes $[(Cp)Fe(dppe)(C{=}CRR')]^+$ (Ia-c) and $[(Cp)Fe\{P(CH_3)_3\}_2\{C{=}C(CH_3)_2\}]^+$ (Id) are inert to alcohols and water.[3,12c] At higher pH, vinylidene complexes containing a β-hydrogen substituent are deprotonated to the corresponding iron alkynyl complex.[1,3a,4] The isobutenylidene complex Ia,



Ia



IV

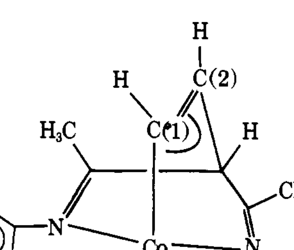
III

(6)

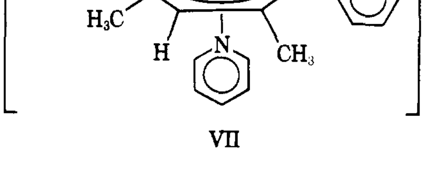
which does not contain a β hydrogen, reacts with hydroxide or other bases by deprotonation of the coordinated dppe ligand, followed by cyclization of the zwitterionic intermediate IV. Evidently, a coordinated phosphine in a cationic transition metal complex can demonstrate enhanced acidity of the α protons. This effect is comparable to the greater acidity of a phosphonium salt relative to its parent phosphine (e.g., $\mathrm{p}K_a(\mathrm{Ph_3PC}H_3{}^+) \approx 15\text{–}20^{20a}$ vs. $\mathrm{p}K_a(\mathrm{Ph_2PC}H_3) \approx 40^{20b}$). Complexes containing R_2PCHR' ligands, similar to intermediate IV, have been isolated and characterized. $[P(CH_3)_3]_3(H)[(CH_3)_2PCH_2]Fe$ appears to be formed by the intramolecular insertion of electron-rich iron(0) into an adjacent P–C–H bond.[21] Lithiated phosphines reacted with metal halides to form $\{[(Ph_2P)_2CH]NiBr\}_2$[22] and $[P(CH_3)_3]_3$-$[(CH_3)_2PCH_2]Co$.[23] Formation of three-membered Pt–P–C rings in 1-[(P-*n*-$(C_3H_7)_3$)Pt(P-*n*-$(C_3H_7)_2$CH-CH_2CH_3)]-2-C_6H_5-1,2-(σ-$B_{10}C_2H_{10}$)[24a] and related carborane complexes[24b,c] was ascribed to internal C–H metalation promoted by the bulky carboranyl group.[24d]

The coordinated carbonyl in $[(Cp)Fe(dppe)(CO)]^+$ (V), which is isoelectronic with Ia, is similarly unreactive toward hydroxide, whereas $[(Cp)Fe(PPh_3)(CO)_2]^+$ reacts with potassium hydroxide to form a stable hydroxycarbonyl complex $(Cp)Fe(PPh_3)(CO)(COOH)$.[25] In fact, the ionic hydroxide salt [(Cp)Fe(dppe)(CO)][OH] can be isolated.[25] The low electrophilicity of the metal-bonded carbon atom in complexes Ia–d and V relative to their carbonyl-containing congeners can be attributed to the better electron-donor capability of phosphine ligands, which in turn permits more effective metal to vinylidene (or carbonyl) π donation of electron density. The lack of reactivity of *trans*-$[Fe(depe)_2Cl(C{=}CHPh)]^+$ [8,26] toward alcohols can also be rationalized in this way. The fact that the dppe ligand in V is not deprotonated by hydroxide is deserving of further study.

The geometry of the polycyclic ring system of complex III can be compared to two other systems containing M–C (sp^2) linkages in constrained rings. In complex VI,[27] the Mn–C–P angle is reduced to 92.0° owing to the strain in the four-membered chelate ring. In the polycyclic complex VII,[28] the Co–C(1)–C(2) angle is relatively unstrained at 117.6°, since it is involved only in six-membered chelate rings.



VI



VII

To summarize, we have demonstrated that a coordinated phosphine in a cationic transition metal complex can show enhanced acidity at the α protons. The intermediate deprotonated phosphine complex can act as a carbon nucleophile toward another ligand in the coordination sphere of the metal. In complex III, the resulting ferradiphospha[2.1.1]bicyclohexane ring system shows novel geometric and spectroscopic features reflecting torsional strain in the molecule.

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Supplementary Material Available: Structure factors and intermolecular contacts for III (13 pages). Ordering information is given on any current masthead page.

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(13) ^{13}C NMR spectra were recorded with complete proton decoupling and internal deuterium lock. Generally, over 10 000 pulses were required to resolve quaternary carbon signals using nearly saturated (0.1–0.5 M) samples.
(14) "International Tables for X-ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1975: (a) Table 2.3.1, pp 149–150; (b) Table 2.2B, pp 99–101.
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only in the presence of excess carboranyllithium it is possible that the deprotonation of a coordinated phosphine is responsible for their formation.

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Synthesis of Triiron Carbonyl Cluster Complexes Containing Isomeric Triply Bridging Acimidoyl or Alkylidenimido Group Derived from the Reduction of Organic Nitriles[1]

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Abstract: Reaction of various iron carbonyls such as $[Fe_2(CO)_8]^{2-}$ (**1**) in the presence of $[W(CO)_5I]^-$, $[HFe_3(CO)_{11}]^-$ (**2**), or $Fe(CO)_5$ in the presence of NaI with refluxing nitriles gives $[Fe_3(RC{=}NH)(CO)_9]^-$ (**3**) and $[Fe_3(N{=}CHR)(CO)_9]^-$ (**4**) (**a**, R = CH_3; **b**, R = Ph; **c**, R = *n*-Pr). These products contain triply bridging acimidoyl or alkylidenimido groups and may be protonated to give the neutral complexes $HFe_3(RC{=}NH)(CO)_9$ (**5**) and $HFe_3(N{=}CHR)(CO)_9$ (**6**), respectively. Deprotonation of **6a** gives pure **4a** but deprotonation of **5a** gives either pure **3a** or a mixture of both **3a** and **4a**, depending on the base employed. Anions **3a** and **4a** do not interconvert but the neutral complex **5a** isomerizes irreversibly to **6a** at 65 °C. The complexes have been characterized by infrared, ^1H NMR, mass spectroscopy, and single-crystal X-ray structure determination (see paper immediately following). The C-N stretching absorptions of **5a** and **6a** have been identified at 1353 and 1325 cm^{-1}, respectively. An intramolecular H/D exchange is observed for monodeuterated complex **6a**: $DFe_3(N{=}CHCH_3)(CO)_9 \rightleftharpoons HFe_3(N{=}CDCH_3)(CO)_9$ ($CDCl_3$, 35 °C). For this exchange, $k_f = 6 \times 10^{-4}\ s^{-1}$ and $K_{eq} = 1.2 \pm 0.2$. Complex **5a** forms hydrogen-bonded adducts via the N-H hydrogen with a variety of bases. The average shift in ν_{CO} upon adduct formation is correlated with the base strength.

Introduction

The π coordination chemistry of ligands containing carbon-carbon multiple bonds is vast.[2] In contrast, the π coordination chemistry of ligands containing carbon-nitrogen multiple bonds is limited, primarily owing to the preferential formation of σ-bonded adducts. Thus, imine, nitrile, alkylidenimino ($N{=}CR_2$), and pyridine ligands form nitrogen-bonded adducts,[3] while isonitriles form carbon-bonded adducts.[4] Although a few π-bonded nitriles[3,5] and heteroaromatics[3] are known, π bonding is more common when there are no lone pairs present on nitrogen such as in the iminium[6] $[R_2C{=}NR_2]^+$, nitrilium (iminoacyl),[7] $[RC{\equiv}NR]^+$, and keteniminium[3,8] $[R_2C{=}C{=}NR_2]^+$ cations.

In theory the use of clusters should provide a means for synthesizing complexes of π coordinated ligands containing carbon-nitrogen multiple bonds or, for that matter, other hetero-unsaturated linkages such as C=O or N=N. The presence of several metal atoms in the cluster allows for a greater diversity of bonding interactions than is possible for an isolated metal atom.[9] This is demonstrated by the increasingly rich cluster chemistry of unsaturated hydrocarbon ligands.[10] In the case of a hetero-unsaturated ligand, one metal could be used to tie up the heteroatom lone pair through a σ bond, permitting one (or more) other metal atom(s) to coordinate in a π fashion to the ligand multiple bond.[11] In practice, a number of clusters are known which contain σ-bonded nitrile,[12] pyridine,[13] isonitrile,[12] acimidoyl ($R\dot{C}{=}\dot{N}R$),[13] or alkylidenimido ($:\dot{N}{=}CR_2$),[14] and *C,C*-iminylidenium ($\cdot\dot{C}{=}NR_2$)[13,15] ligands. However, we are aware of only a few cases where π coordination is present in addition to σ coordination, namely, in $HOs_3(RC{=}NR')(CO)_9$ (R = H, R' = CH_3;[13a] R = Ph, R' = CH_3;[13b] R = H, R' = Ph)[13c] and $Ni_4(CNR)_7$.[16]

Since to date most studies of hydridocarbonyl cluster compounds have involved the precious metals (primarily Re, Ru, and Os), we have been attempting to extend our studies to that of the more common metals. An unexpected result has led us to the preparation of several novel iron cluster complexes containing π-bonded acimidoyl or alkylidenimido groups; see Scheme I. Because the clusters reported here can be readily prepared in gram quantities, it has been possible to study a wide range of their physical and chemical properties. These results are detailed in this and the following papers.[1]

Results

Synthesis of the Neutral Complexes $HFe_3(CH_3C{=}NH)(CO)_9$ (5a) and $HFe_3(N{=}CHCH_3)(CO)_9$ (6a). One approach to the synthesis of cluster complexes is the reaction of a metal anion with a complex which contains a readily displaceable ligand. For example, the reaction of $[Mn(CO)_5(CH_3CN)]^+$ with $[Fe_2(CO)_8]^{2-}$ (**1**) gives $[MnFe_2(CO)_{12}]^-$.[17] By analogy we treated $[W(CO)_5I]^-$ with **1** in refluxing acetonitrile, hoping to obtain $[WFe_2(CO)_{12}]^{2-}$. No mixed metal products were obtained; however, a mixture of anions (later shown to consist of $[Fe_3(CH_3C{=}NH)(CO)_9]^-$ (**3a**) and $[Fe_3(N{=}CHCH_3)(CO)_9]^-$ (**4a**)) together with $W(CO)_3(CH_3CN)_3$ was produced. In order to facilitate separation and product identification, the anionic species were acidified with phosphoric acid. The resulting neutral material was readily resolved into two components by column chromatography. With the aid of a variety of spectroscopic data (Table I and vide infra) it was possible to deduce that the two complexes are $HFe_3(CH_3C{=}NH)(CO)_9$ (**5a**, 31% yield) and $HFe_3(N{=}CHCH_3)(CO)_9$ (**6a**, 8% yield). The structures of both of these represented in Scheme I have been confirmed by single-crystal

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