cation of high-pressure NMR techniques.[21,22] In addition, the significance of the various reaction routes in (5) could be resolved by performing a [THF] dependence study in which the solutions are diluted with a noncoordinating solvent.[22] In the investigated systems we are dealing with a fine balance of molecular size, steric hindrance, and nucleophilicity in determining the nature of the substitution process. Such mechanistic details could not be resolved on the basis of the thermal activation parameters only.

Acknowledgment. We gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft, Fonds der Chemischen Industrie, and the Volkswagen-Stiftung.

Registry No. $Cr(CO)_5THF$, 15038-41-2; $Mo(CO)_5THF$, 53248-43-4; $W(CO)_5THF$, 36477-75-5; $P(OC_2H_5)_3$, 122-52-1; $P(C_6H_5)_3$, 603-35-0; piperidine, 110-89-4.

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Synthesis and Properties of the Novel η^4-Trimethylenemethane Compounds $\{\eta^4\text{-}C(CH_2)_3\}Fe(CO)_2L$ (L = Tertiary Phosphines, *tert*-Butyl Isocyanide)

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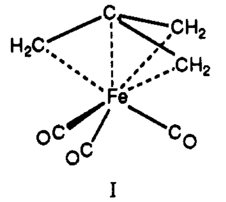
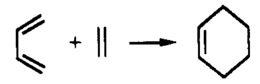
The new compounds $\{\eta^4\text{-}C(CH_2)_3\}Fe(CO)_2L$ ((TMM)$Fe(CO)_2L$; L = PPh_3, $PMePh_2$, PMe_2Ph, $PCyPh_2$, PCy_2Ph, PCy_3, P(*m*-xylyl)$_3$, PBz_3, *t*-BuNC) have been synthesized by substitution of CO on $\{\eta^4\text{-}C(CH_2)_3\}Fe(CO)_3$ and are found to be surprisingly stable with respect to thermolysis and air oxidation. All have been characterized by IR and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ spectroscopy, and some electrochemically; fluxional behavior involving TMM rotation is observed for several of the compounds. The X-ray crystal structure of (TMM)$Fe(CO)_2PCy_2Ph$ shows that the TMM ligand assumes a typical "umbrella-like" mode of coordination; the internal TMM ligand bond angles and distances differ little from those of other TMM–iron compounds, although the Fe–C distance of the methylene group "trans" to phosphorus is marginally longer than the other two iron–methylene distances.

Introduction

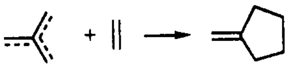
The short-lived, highly reactive biradical trimethylenemethane (TMM) was first stabilized by coordination to an $Fe(CO)_3$ fragment in 1966, yielding the novel compound $\{\eta^4\text{-}C(CH_2)_3\}Fe(CO)_3$ (I, TMMFe$(CO)_3$).[1] Since then, a large number of derivatives in which one or more hydrogen atoms of the TMM are substituted have also been reported,[2] and the chemistry of these compounds has been extensively reviewed.[3] Much of the interest in coordinated TMM stems from its potential use in [3 + 2] cycloadditions resembling Diels–Alder processes, an analogy prompted by the close topological similarities in the frontier orbitals of TMM and a cis-conjugated diene[4] and accentuated in eqs 1 and 2. Thus, although all attempts to react (TMM)$Fe(CO)_3$ with dienophiles have proven unsuccessful,[5] a number of η^3-TMM complexes of palladium have been found to participate in a variety of [3 + 2] cycloaddition reactions.[6] The low reactivity of (TMM)$Fe(CO)_3$ may be understood in terms of overlap arguments,[7] but may also, if the above-mentioned analogy with the Diels–Alder reaction is valid, be a result of the compound being too electron poor. Gas-phase valence-electron photoelectron data for this compound show that the first ionization potential is 8.32 eV,[8] and the reported values of ν(CO) are relatively high (2061, 1995 cm^{-1} in hexane[1]).



I



(1)



(2)

It follows that reactivity might be introduced into the system by substituting one or more of the carbonyl groups by tertiary phosphines, and we have investigated briefly the chemistry of the electron-rich compound (η^4-TMM)$Fe(PMe_3)_3$.[9] Unfortunately, attempts to react this compound with a variety of reagents utilized previously[6] resulted in the formation only of 1,4-dimethylenecyclohexane, formally a dimer of the TMM diradical.[10]

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Table I. Infrared Spectra (ν_{CO} Region) of the Complexes (TMM)Fe(CO)$_2$L

L	ν(CO), cm^{-1} [a]
PPh_3	1997, 1941
$PMePh_2$	1994, 1938
PMe_2Ph	1992, 1935
$PCyPh_2$	1991, 1987, 1934, 1931
PCy_2Ph	1992, 1988, 1933, 1930
PCy_3	1986, 1928
P(*m*-xylyl)$_3$	1994, 1938
PBz_3	1991, 1933
t-BuNC	2005, 1959

[a] In petroleum ether, bp 30–60 °C.

Table II. ^{1}H NMR Spectra of the Complexes (TMM)Fe(CO)$_2$L

L	δ(TMM): *J*, Hz	δ(L): *J*, Hz
PPh_3 [a]	2.05 (s, H_c)	7.0–7.6 (m, Ph)
	1.80 (d, J_{HH} 3.7, H_b)	
	1.07 (dd, J_{HH} 3.7, J_{PH} 9.4, H_a)	
$PMePh_2$ [c]	1.90 (s, H_c)	6.8–7.5 (m, Ph)
	1.70 (d, J_{HH} 3.8, H_b)	1.57 (d, J_{PH} 7.5)
	1.05 (dd, J_{HH} 3.8, J_{PH} 10.4, H_a)	
PMe_2Ph [c]	1.67 (s, H_c)	6.9–7.4 (m, Ph)
	1.58 (d, J_{HH} 3.8, H_b)	1.28 (d, J_{PH} 8.1)
	1.02 (dd, J_{HH} 3.8, J_{PH} 11.0, H_a)	
$PCyPh_2$ [b]	1.69 (s, H_c)	7.3–7.6 (m, Ph)
	1.55 (d, J_{HH} 2.4, H_b)	0.83–2.23 (m, Cy)
	0.78 (dd, J_{HH} 2.4, J_{PH} 9.0, H_a)	
PCy_2Ph [b]	obscured	1–2.5 (m, Cy)
PCy_3 [b]	obscured	0–2.4 (m, Cy)
P(*m*-xylyl)$_3$ [b]	1.81 (s, H_c)	6.8–7.3 (m, Ph)
	1.55 (d, J_{HH} 3.7, H_b)	2.20 (s, Me)
	0.83 (dd, J_{HH} 3.7, J_{PH} 9.2, H_a)	
PBz_3 [c,d]	1.62 (d, J_{HH} 3.7 H_b)	6.9–7.4 (m, Ph)
	1.42 (s, H_c)	3.04 (d, J_{PH} 7.8, CH_2)
	0.97 (dd, J_{HH} 3.7, J_{PH} 9.3, H_a)	
t-BuNC [b]	1.82 (s, H_c)	1.40 (s, Me)
	1.65 (d, J_{HH} 4.2, H_b)	
	1.45 (d, J_{HH} 4.2, H_a)	

[a] In CD_2Cl_2. [b] In $CDCl_3$. [c] In toluene-d_8. [d] At 265 K.

We have consequently undertaken the synthesis of partially substituted compounds of the type (TMM)Fe(CO)$_2$L (L = *t*-BuNC, tertiary phosphine); only PF_3 derivatives had previously been reported.[11] It was anticipated that tertiary phosphine substituted compounds might not only be significantly more electron rich, but that sufficient asymmetry might also be introduced into the coordinated TMM so that overlap requirements[7] might also be satisfied. The results of our investigations into the synthesis and characterization of a series of new compounds are presented in this paper.

Table III. $^{13}C\{^1H\}$ NMR Spectra of the Complexes (TMM)Fe(CO)$_2$L

L	δ (TMM) (*J*, Hz)	δ (L) (*J*, Hz)
PPh_3 [a]	107.0 (s, C_1)	128–138 (m, Ph)
	57.4 (d, J_{PC} 4.6, C_3)	217.9 (d, J_{PC} 10.6, CO)
	46.6 (d, J_{PC} 3.6, C_2)	
$PMePh_2$ [b]	106.6 (s, C_1)	128–138 (m, Ph)
	55.4 (d, J_{PC} 4.8, C_3)	20.5 (d, J_{PC} 28.1, Me)
	46.5 (d, J_{PC} 9.1, C_2)	217.1 (d, J_{PC} 11.2, CO)
PMe_2Ph [b]	107.1 (s, C_1)	127–141 (m, Ph)
	54.4 (d, J_{PC} 4.1, C_3)	19.5 (d, J_{PC} 28.3, Me)
	46.4 (d, J_{PC} 9.3, C_2)	217.5 (d, J_{PC} 10.5 CO)
$PCyPh_2$ [b]	106.7 (s, C_1)	127–136 (m, Ph)
	56.0 (br s, C_3)	26–41 (m, Cy)
	46.4 (d, J_{PC} 8.7, C_2)	218.4 (d, J_{PC} 10.3, CO)
PCy_2Ph [c]	106.1 (s, C_1)	127–135 (m, Ph)
	52.4 (d, J_{PC} 3.7, C_3)	26–40 (m, Cy)
	48.5 (d, J_{PC} 11, C_2)	219.7 (d, J_{PC} 11.3, CO)
PCy_3 [b]	104.6 (s, C_1)	26–39 (m, Cy)
	50.7 (d, J_{PC} 7.0, C_3)	219.1 (d, J_{PC} 11, CO)
	48.5 (d, J_{PC} 9, C_2)	
P(*m*-xylyl)$_3$ [b]	106.6 (s, C_1)	130–138 (m, Ph)
	57.1 (d, J_{PC} 10.0, C_3)	21.0 (s, Me)
	45.7 (d, J_{PC} 12.0, C_2)	218 (d, J_{PC} 6, CO)
PBz_3 [d]	105 (s, C_1)	126–134 (m, Ph)
	53.3 (d, J_{PC} 5.1, C_3)	37.0 (d, J_{PC} 16, CH_2)
	47.8 (d, J_{PC} 8.4, C_2)	217 (d, J_{PC} 10, CO)
t-BuNC [b]	106.2 (s, C_1)	34.1 (s, *C*Me$_3$)
	53.5 (s, C_3)	30.8 (s, Me)
	47.6 (s, C_2)	

[a] In CD_2Cl_2. [b] In $CDCl_3$. [c] In acetone-d_6. [d] At 280 K.

Table IV. $^{31}P\{^1H\}$ NMR Spectra of the Complexes (TMM)Fe(CO)$_2$L

L	δ [c]	L	δ [c]
PPh_3	74.3 [a]	PCy_2Ph	44.8 [b]
$PMePh_2$	53.9 [b]	PCy_3	71.4 [b]
PMe_2Ph	34.7 [a]	P(*m*-xylyl)$_3$	74.5 [b]
$PCyPh_2$	38.5 [b]	PBz_3	59.7 [b]

[a] CD_2Cl_2. [b] C_6D_6. [c] External H_3PO_4, solvent.

Experimental Section

Syntheses were performed under N_2 atmosphere on a vacuum line, by using Schlenk techniques and dried, deaerated solvents. IR spectra were recorded on a Bruker IFS-85 FT-IR spectrophotometer (see Table I for ν(CO) data), NMR spectra on Bruker ACF-200 and AM-400 FT-NMR spectrometers (Tables II–IV). Elemental Analyses were carried out by Canadian Microanalytical Services, Delta, BC, Canada.

Cyclic voltammograms were obtained by using a three-electrode cell system, and a Princeton Applied Research Model 174A Polarographic Analyzer coupled to a Chemtrix Type 800A waveform source and a Hewlett Packard 7005B x-y recorder. Scan rates used in the investigations ranged from 0.020 to 0.400 V s^{-1}. Solutions containing samples at millimolar concentrations and 0.1 M Et_4NCl supporting electrolyte were used. Cyclic voltammograms of the sample solutions were obtained at multiple scan rates by using a platinum disk working electrode (A = 3.14 × 10^{-2} cm^2) which was cleaned before each series of runs. The Pt disk electrode potential was referred to a Ag/AgCl/0.1 M Et_4NCl reference electrode, with a platinum wire auxiliary electrode completing the potentiostatic circuit. Results of the electrochemical experiments are summarized in Table V.

The compounds PPh_3 (Strem), $PMePh_2$ (Strem), PMe_2Ph (Strem), PCy_2Ph (M&T), $PCyPh_2$ (M&T), PBz_3 (M&T), P(*m*-xylyl)$_3$ (M&T), PCy_3 (Maybridge Chemical Co. Ltd.), 3-chloro-2-(chloromethyl)-1-propene (Aldrich), and *tert*-butyl isocyanide (Aldrich) were used as received, and chromatography was performed utilizing silica gel 60 (Merck). $Na_2Fe(CO)_4$[12] and $Me_3NO{\cdot}2H_2O$[13,14] were prepared as in the literature.

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Table V. Electrochemical Data for the Compounds (TMM)Fe(CO)$_2$L

(a)

L	$(E_p)_a$, V	$(E_p)_c$, V	ΔE_p, V	scan rate, mV/s^{-1}
PPh_3	0.300	0.236	0.064	60–400
$PMePh_2$	0.270	0.195	0.075	50–90
PMe_2Ph	0.257	0.183	0.074	20–50
$PCyPh_2$	0.340	0.276	0.064	60–270
PCy_2Ph	0.371	0.308	0.063	40–400
PBz_3	0.270	0.199	0.071	25–60
CO	0.299	0.239	0.060	50–160
Cp_2Fe	0.845	0.768	0.077	50

(b)

L	$(i_p)_a$, μA	$(i_p)_c$, μA	$(i_p)_a(i_p)_c$	k, A L mol^{-1} (V s^{-1})$^{-1/2}$
PPh_3	0.32	0.30	0.94	0.0012
$PMePh_2$	0.74	0.66	0.89	0.0026
PMe_2Ph	0.76	0.60	0.79	0.0030
$PCyPh_2$	0.40	0.31	0.78	0.0015
PCy_2Ph	0.19	0.15	0.79	0.0008
PBz_3	0.72	0.62	0.86	0.0031
Cp_2Fe	1.48	1.18	0.80	0.0032

Synthesis of the Complexes (TMM)Fe(CO)$_2$L. In general, (TMM)Fe(CO)$_3$ was generated by treating a suspension of ~0.5 g of $Na_2Fe(CO)_4$ (2.4 mmol) in 20 mL of THF with ~0.35 mL of $H_2C{=}C(CH_2Cl)_2$ (~3.0 mmol). The mixture was stirred at ambient temperature for 1 h, by which time monitoring by IR spectroscopy indicated that formation of (TMM)Fe(CO)$_3$ had ceased. The solution was then treated with ~2.8 g of solid $Me_3NO{\cdot}2H_2O$ (~25 mmol), and the mixture was refluxed for 30 min. The desired ligand (~5 mmol) was then added, and the mixture was refluxed overnight. Complete reaction of the (TMM)Fe(CO)$_3$ was confirmed by disappearance of the ν(CO) at 2059 cm^{-1} in the IR spectrum, and the muddy-looking reaction mixture was placed on a 15 × 1 cm silica column. The reaction mixture was eluted with petroleum ether (bp 30–60 °C), the fast-running yellow band being collected. The resulting yellow solution was concentrated in vacuo, and the material obtained was dissolved in a minimum volume of CS_2. The resulting CS_2 solution was in turn chromatographed through silica, and the faster running band, typically pale yellow, was again collected and concentrated to give the desired product in 25–75% yield. Analytically pure samples were obtained by dissolving the compounds in 5–10 mL of petroleum ether (bp 30–60 °C) and allowing slow evaporation under a stream of nitrogen. Appearances of the new compounds were as follows: (TMM)Fe(CO)$_2$PPh$_3$, yellow solid, mp 168–170 °C; TMMFe(CO)$_2$PMePh$_2$, pale yellow oil; (TMM)Fe(CO)$_2$PMePh$_2$, yellow oil; TMMFe(CO)$_2$PCyPh$_2$, pale orange solid, mp 127–129 °C; (TMM)Fe(CO)$_2$PCy$_2$Ph, pale orange solid, mp 128–129 °C; (TMM)Fe(CO)$_2$PCy$_3$, pale yellow solid, mp 171–173 °C; TMMFe(CO)$_2$P(*m*-xylyl)$_3$, pale yellow solid, mp 175–177 °C; TMMFe(CO)$_2$PBz$_3$, pale yellow solid, mp 175–177 °C; (TMM)Fe(CO)$_2$(*t*-BuNC), pale yellow solid, mp 85–86 °C. Anal. Calcd for (TMM)Fe(CO)$_2$PPh$_3$, $C_{24}H_{21}FeO_2P$: C, 67.31; H, 4.94; Found: C, 67.22; H, 5.03. Calcd for (TMM)Fe(CO)$_2$PMePh$_2$, $C_{19}H_{19}FeO_2P$: C, 62.32; H, 5.23; Found: C, 62.38; H, 5.16. Calcd for (TMM)Fe(CO)$_2$PMe$_2$Ph $C_{14}H_{17}FeO_2P$: C, 55.29; H, 5.63; Found: C, 55.64; H, 5.93. Calcd for (TMM)Fe(CO)$_2$PCyPh$_2$, $C_{24}H_{27}FeO_2P$: C, 66.37; H, 6.26; Found: C, 66.50; H, 6.38. Calcd for (TMM)Fe(CO)$_2$PCy$_2$Ph, $C_{24}H_{33}FeO_2P$: C, 65.46; H, 7.55; Found: C, 65.65; H, 7.50. Calcd for (TMM)Fe(CO)$_2$PCy$_3$, $C_{24}H_{39}FeO_2P$: C, 64.57; H, 8.81; Found: C, 63.54; H, 8.67. Calcd for (TMM)Fe(CO)$_2$P(*m*-xylyl)$_3$, $C_{30}H_{33}FeO_2P$: C, 70.32, H, 6.49; Found: C, 70.32; H, 6.66. Calcd for (TMM)Fe(CO)$_2$PBz$_3$, $C_{27}H_{27}FeO_2P$: C, 68.95; H, 5.79; Found: C, 68.71; H, 5.83. Calcd for (TMM)Fe(CO)$_2$(*t*-BuNC), $C_{11}H_{15}FeNO_2$: C, 53.04; H, 6.07; N, 5.62; Found: C, 52.31; H, 6.06; N, 5.02.

Table VI. Crystallographic Data for (TMM)Fe(CO)$_2$PCy$_2$Ph

mol formula	$C_{40}H_{33}FeO_2P$
mol wt	440.34
space group	$P2_1/n$ (no. 14)
a, Å	13.639 (6)
b, Å	11.296 (6)
c, Å	15.661 (6)
β, deg	110.60 (5)
V, Å^3	2264.0
Z	4
D, g cm^{-3}	1.292
μ	0.772
T, K	292
crystal dimensions, mm	0.15 × 0.25 × 0.40
F(000)	936
λ (Mo Kα)	0.710732
2θ range scanned (deg)	1.0–40.0
$\sin \theta/\lambda$ max	0.480
h,k,l range scanned	$0 \rightarrow 13$, $0 \rightarrow 10$, $-14 \rightarrow 14$
no. of unique reflections	2101
no. of observed reflections	1676
final R, R_w	0.033, 0.034
largest shift/error in final least-squares cycle, δ/σ	0.002
max and min electron density in final difference Fourier map	0.406, -0.287

X-ray Crystal Structure of (TMM)Fe(CO)$_2$PCy$_2$Ph. Yellow crystals of (TMM)Fe(CO)$_2$(PCy$_2$Ph) were obtained by slow evaporation of a solution of the compound in petroleum ether (bp 30–60 °C) at ambient temperature, and a suitable crystal was mounted with epoxy on a glass fiber. Diffraction data were collected on an Enraf-Nonius CAD-4 diffractometer by using Mo Kα graphite-monochromated X-ray radiation, and the unit cell was determined from a list of 25 well-centered reflections. A $\omega/2\theta$ data collection was carried out at room temperature, with intensity and orientation standards showing no significant variation over the length of the data aquisition period. Systematic extinctions confirmed the space group determination.

The data were corrected for Lorentz and polarization effects; absorption corrections were not considered necessary. The structure was solved through direct methods on a Sun Sparc Station with use of the XTAL 3.0 program package,[15] with all atoms, including the H atoms, being located. Isotropic refinement[16] was carried out with the heavy-atom positions. Hydrogen atoms were assigned the isotropic temperature factor associated with the parent atoms and their locations were not refined. Full-matrix least-squares refinement of positional and thermal parameters included all reflections having $I > 3\sigma(I)$. In the final cycles, a full-matrix refinement involving anisotropic temperature factors for all heavy atoms converged to give agreement factors of $R = 0.033$ and $R_W = 0.034$. Details related to the crystal data, intensity measurements, and the final refinement parameters are summarized in Table VI, and pertinent bond lengths and angles are in Table VII. Final positional and equivalent thermal parameters are deposited as Supplementary Material.

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[16] The function being minimized was $\sum_h w(|F_o| - |F_c|)^2$, where $w^{-1} = \sigma F_o$.

Table VII. Selected Bond Lengths (Å) and Angles (deg) of (TMM)Fe(CO)$_2$PCy$_2$Ph

	Bond Lengths		
Fe–P	2.263 (2)	C1–01	1.157 (8)
Fe–C1	1.749 (6)	C2–02	1.156 (7)
Fe–C2	1.758 (6)	C3–C4	1.41 (1)
Fe–C3	1.934 (5)	C3–C5	1.421 (9)
Fe–C4	2.128 (6)	C3–C6	1.412 (9)
Fe–C5	2.129 (6)	P–C7	1.855 (5)
Fe–C6	2.138 (5)	P–C13	1.850 (9)
		P–C19	1.859 (4)
	Bond Angles		
P–Fe–C1	97.5 (2)	C3–Fe–C4	40.3 (3)
P–Fe–C2	95.4 (2)	C3–Fe–C5	40.6 (2)
C1–Fe–C2	98.0 (2)	C3–Fe–C6	40.2 (3)
P–Fe–C3	124.8 (2)	C4–C3–C5	113.8 (6)
C1–Fe–C3	117.4 (3)	C4–C3–C5	116.9 (5)
C2–Fe–C3	118.3 (3)	C5–C3–C6	115.3 (7)
Fe–C1–01	174.9 (4)	Fe–C2–02	178.7 (5)

Results and Discussion

Syntheses. The new compounds (TMM)Fe(CO)$_2$L were synthesized in yields of up to 75% based on Na$_2$[Fe(CO)$_4$] used via the sequence of reactions shown in eqs 3 and 4. Although previous workers have reported better

$$\mathrm{Na_2[Fe(CO)_4] + H_2C{=}C(CH_2Cl)_2 \rightarrow (TMM)Fe(CO)_3} \tag{3}$$

$$\mathrm{(TMM)Fe(CO)_3 + Me_3NO + L \rightarrow (TMM)Fe(CO)_2L + NMe_3 + CO_2} \tag{4}$$

yields of (TMM)Fe(CO)$_3$ utilizing Fe$_2$(CO)$_9$,[1] we find that the latter route also results in the significant formation of Fe(CO)$_5$, which is very difficult to separate from the desired, volatile product (TMM)Fe(CO)$_3$. In contrast, the Na$_2$Fe(CO)$_4$ method utilized here appears to result in the formation of sufficiently low quantities of Fe(CO)$_5$ that the latter is readily destroyed by the addition of Me$_3$NO·2H$_2$O[14] and hence does not interfere in the subsequent synthetic process. The compound (TMM)Fe(CO)$_3$ appears to be inert to Me$_3$NO·2H$_2$O, and only undergoes substitution in the presence of added ligand.[14]

Upon disappearance of (TMM)Fe(CO)$_3$, isolation of the products requires two separations on silica gel. The first, essentially a filtration, efficiently removes unreacted, insoluble Me$_3$NO, as well as some of the excess ligand. The second, using CS$_2$ as an eluent, removes several of the unreacted phosphine ligands as polar adducts of the type R$_3$P·CS$_2$.[17] The substituted products are either yellow to orange solids or yellow oils (L = PMe$_2$Ph, PMePh$_2$). All are surprisingly air stable, exhibiting considerable robustness to air even in solution.

X-ray Structure of (TMM)Fe(CO)$_2$PCy$_2$Ph. The structure of (TMM)Fe(CO)$_2$PCy$_2$Ph is shown in Figure 1, and relevant bond distances and angles are listed in Table VII. As in the structures of (TMM)Fe(CO)$_3$ and a number of TMM-substituted derivatives which have been reported,[9,18] the TMM ligand of (TMM)Fe(CO)$_2$PCy$_2$Ph assumes an "umbrella-like" arrangement, with the central carbon atom closer to the iron than are the methylene carbon atoms and with the latter staggered with respect to the other three ligands on the iron. The molecular dimensions of (TMM)Fe(CO)$_2$PCy$_2$Ph are rather similar to those of the acyclic phenyl-substituted compound {η^4-(PhCH)C(CH$_2$)$_2$}Fe(CO)$_3$,[18] which seems to be the only such compound for which the TMM ligand is not cyclic in nature and for which an X-ray crystal structure is known in detail, and to those of the 17-electron, cationic trisphosphine complex [(TMM)Fe(PMe$_3$)$_3$](CF$_3$SO$_3$).[9] Comparing (TMM)Fe(CO)$_2$PCy$_2$Ph and {η^4-(PhCH)C(CH$_2$)$_2$}Fe(CO)$_3$, the Fe–CO bond lengths of the latter are slightly longer, presumably a result of decreased π back-donation, while the η^4 ligand C–C distances are slightly shorter. The Fe–C distances of the two compounds differ surprisingly little, although the methylene carbon atom "trans" to phosphorus in (TMM)Fe(CO)$_2$PCy$_2$Ph lies farther from the iron than do the other two methylene carbon atoms of this compound. Interestingly, the Fe–P bond distances of (TMM)Fe(CO)$_2$PCy$_2$Ph and of [(TMM)Fe(PMe$_3$)$_3$](CF$_3$SO$_3$) are essentially identical in length.

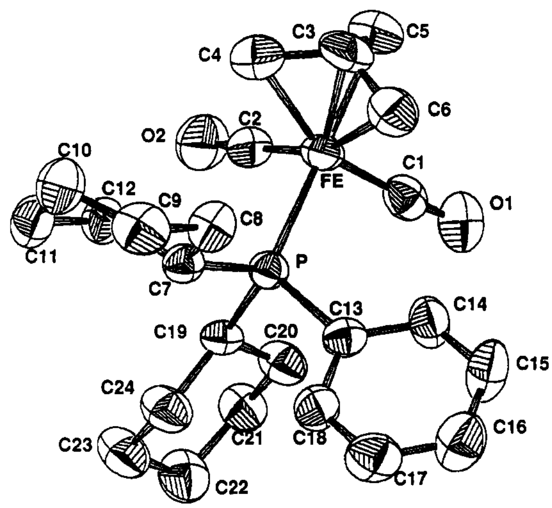
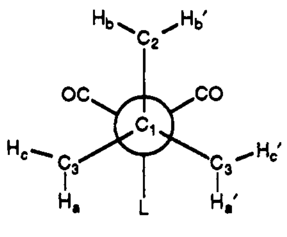


Figure 1. ORTEP drawing of (TMM)Fe(CO)$_2$PCy$_2$Ph.

IR, ^{1}H NMR, ^{13}C{^{1}H} NMR, and ^{31}P{^{1}H} NMR Spectroscopy. All of the new compounds exhibit pairs of ν(CO) in their IR spectra (Table I), as anticipated for dicarbonyl compounds. In some cases shoulders were observed on the main ν(CO), possibly indicating the presence of conformational isomers. Several staggered conformations could result from rotation about the Fe–C bonds, although the X-ray crystal structure of (TMM)Fe(CO)$_2$PCy$_2$Ph indicates that, for this compound, only a single such conformation occurs in the solid state.

The ^{1}H NMR data for the new compounds are listed in Table II. The parent compound, (TMM)Fe(CO)$_3$, contains six equivalent protons, the resonance of which appears as a broad singlet at δ 2.0 in a variety of solvents. As indicated in the Newman diagram of II, the equivalence is lost upon substitution of a carbonyl group, and three different pairs of ^{1}H sites in the TMM ligand, H$_a$, H$_b$, and H$_c$, ensue if rotation of the TMM relative to the other ligands is slow on the NMR time scale. Although little is in fact known about fluxionality in such systems, TMM-substituted compounds (RTMM)Fe(CO)$_3$ (R = CHOHMe, CHMeOAc, Et)[19] and PF$_3$-substituted compounds (TMM)Fe(CO)$_n$-



II

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$(PF_3)_{3-n}$[11] are fluxional only at high temperatures, observations which have been rationalized theoretically.[4]

In fact, three TMM ^1H resonances are observed for most of the compounds at room temperature, suggesting that the TMM ligands do not undergo rapid rotation about the primary axis of the molecule. Assignments are facilitated by the observation of "*W*" coupling of certain pairs of TMM protons, as reported for the compound (TMM)Os$(CO)_2PPh_3$.[20] As shown in II, the nonequivalent H_a and H_b' (H_a' and H_b) are linked through "*W*"-shaped bond patterns, resulting in significant long-range spin–spin coupling. Geminal couplings and other long range couplings are too small to be resolved, and thus the observed ^1H NMR resonance patterns consist of a singlet, attributed to H_c (and H_c'), and two doublets, attributed to H_a (and H_a') and H_b (and H_b'). If the ligand L is a phosphine, the $H_a(H_a')$ doublet is further split, appearing as a doublet of doublets. All three resonances appear between δ 0 and δ 2.5, and their discrete existence at room temperature underscores the nonfluxional nature on the NMR time scale of most of the compounds. Interestingly, the ^1H NMR spectrum of the tribenzylphosphine complex exhibited rather broad TMM resonances at room temperature, suggesting the possibility of fluxional behavior in this case (see below).

The $^{13}C\{^1H\}$ NMR data are listed in Table III. The pattern of resonances arising from the (TMM)$Fe(CO)_2$ group are remarkably consistent and display the broad characteristics described for many other TMM complexes.[3b] As is seen in Table III, the central carbon (C_1) of the TMM group appears at δ 106 ± 2, the equivalent carbons (labeled C_3) appear as either a doublet or a broadened singlet in the region δ 50–58, while C_2 appears as a doublet at δ 45–49. Again, the existence of discrete signals for C_2 and C_3 provides support for a nonfluxional TMM group except for the possible exception of (TMM)$Fe(CO)_2PBz_3$. For this compound, only one weak, broad CH_2 resonance was observed at room temperature, a result consistent with the above-mentioned ^1H NMR spectrum and suggesting the existence of an exchange process (see below). In all cases, the resonances of the CO groups appear as doublets at δ 218 ± 1.

The above ^1H and ^{13}C assignments were confirmed by a proton–carbon heteronuclear correlation experiment[21] with the compound (TMM)$Fe(CO)_2PMePh_2$, chosen because of its well-resolved ^1H spectrum. In this experiment, the C_3 resonance gave rise to two cross peaks, correlating to the resonances assigned to H_c (and H_c') and H_a (and H_a') of the TMM group. The C_2 resonance gave rise to a single crosspeak, correlating with the doublet of doublets attributed to H_b (and H_b') in the proton spectrum. The connectivities for (TMM)$Fe(CO)_2$(*t*-BuNC) were simiarly established. The $^{31}P\{^1H\}$ NMR spectra of new compounds exhibit only single resonances, typically well separated from the signal displayed by the corresponding free PR_3 (Table IV).

TMM Ligand Rotation. Variable-Temperature NMR Spectroscopy. An earlier variable-temperature $^{13}C\{^1H\}$ NMR investigation of the compounds $\{\eta^4\text{-RCHC}(CH_2)_2\}Fe(CO)_3$ (R = COMe, CHOHMe, CHMeOAc, Et)[19] has found that the barriers to rotation of the η^4 ligands are 70–75 kJ mol^{-1}, much larger than observed for many cyclic and acyclic polyenes, and rationalized theoretically on the basis of very significant electronic stabilization of the ground-state structures.[4] Interestingly, it was also predicted that substitution of CO by a tertiary phosphine should result in an increase in the electronic barrier to rotation,[4] and thus our observation of apparent exchange broadening for the tribenzylphosphine complex piqued our curiosity. Interestingly, lowering the temperature resulted in the TMM methylene resonances of both the ^1H and the $^{13}C\{^1H\}$ spectra sharpening considerably, until both exhibited fine structure and spectral patterns typical of the other compounds at room temperature (Tables II and III). Increasing the temperature to above 360 K resulted in eventual coalescence of all methylene proton resonances to a doublet, with J_{PH} = 3.0 Hz, the average of the individual, low-temperature values of J_{PH}. Thus the exchange process does not involve phosphine ligand dissociation, but rather must involve TMM rotation; a barrier to rotation of $\Delta G^* \approx 63$ kJ mol^{-1}, *considerably less* than observed for the tricarbonyl system,[19] was calculated on the basis of coalescence temperatures and broadening of the narrow singlet resonance of H_c. We therefore investigated the variable-temperature ^1H NMR spectra of (TMM)$Fe(CO)_2PMe_2Ph$ and (TMM)$Fe(CO)_2PPh_3$, finding very similar coalescence phenomena and estimates of ΔG^* of 72 and 70 kJ mol^{-1}, respectively. The fluxionality exhibited by this family of compounds may thus be subject to both steric and electronic control; a more detailed investigation of the fluxionality of all of the compounds in the series will be published separately.

Electrochemistry. Cyclic volammograms of the complexes (TMM)$Fe(CO)_3$ and (TMM)$Fe(CO)_2L$ all exhibited quasireversible, one-electron oxidation/reduction couples over the range of scan rates examined. The results are summarized in Table V. The number of electrons involved in each couple was estimated from the difference in the peak potentials for oxidation and reduction in the cyclic voltammograms. For comparison, the electrochemical reaction of ferrocene in acetonitrile was investigated; in this solvent ferrocene is known to undergo a reversible, one-electron charge transfer process at 0.05 V s^{-1}.[22] Ferrocene showed a peak separation of 0.077 V, while the TMM complexes investigated showed separations ranging from 0.063–0.075 V. This similarity in ΔE_p values suggests that the latter compounds undergo a one-electron, quasireversible charge transfer process although the ΔE_p values exceed the 0.059 V value expected for a reversible, one-electron couple.

Our conclusion of near reversibility is supported by the ratios of anodic to cathodic current peak heights, which were found to be near unity for all samples examined; a value of one would be obtained in a perfectly reversible system.[23] Unfortunately, near reversibility is not supported by the comparisons of peak current values; according to theory,[23] the experimental peak current $(i_p)_a$ varies with the bulk concentration of the reacting species, C*, and with the square root of the scan rate, $v^{1/2}$.

$$(i_p)_a = kC^*v^{1/2} \qquad (5)$$

The proportionality constant *k* is dependent on *n*, the number of electrons in the charge transfer step and also on the diffusion coefficient of the reacting species.[23] For a series of compounds undergoing charge transfer processes where *n* = 1, one expects the *k* values to be similar.

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$$k = (i_p)_a / C^* v^{1/2} \qquad (6)$$

As can be seen in Table V, the k values can be broadly categorized into two groups, those for which the observed k value approaches that of ferrocene (L = PMe_2Ph, PBz_3, and $PMePh_2$) and those for which k is appreciably different (PPh_3, $PCyPh_2$, and PCy_2Ph). The phosphines in the latter group all contain three very bulky cyclic groups, and the smaller k values may result from significantly smaller diffusion coefficients for the compounds.

Over a range of scan rates (specified for each complex in Table V), each redox couple displayed an invariant peak potential. Consequently, for the solvent system used, with a maximum attainable oxidation state of +1, the general reaction is expected to be

$$(TMM)Fe(CO)_2L \rightarrow (TMM)Fe(CO)_2L^+ + e^- \qquad (7)$$

One would expect this process to be facilitated by the more electron-donating phosphines, but there is in fact little correlation between electron donation by the phosphine (as evidenced by IR ν_{CO} frequencies) and the mean of the observed $(E_p)_a$ and $(E_p)_c$ (which should approximate the thermodynamic $E°$ values).

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Supplementary Material Available: Tables of fractional coordinates and isotropic displacement parameters for all atoms (3 pages); a listing of calculated and observed structure factors (15 pages). Ordering information is given on any current masthead page.

Cyclic Voltammetric Study of the Metal-Centered Radicals $\{\eta^5\text{-}C_5H_5Cr(CO)_2L\}$ (L = CO, PMe_3, PMe_2Ph, $PMePh_2$, PPh_3) and $\{\eta^5\text{-}C_5Me_5Cr(CO)_3\}$

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The results of a cyclic voltammetry study of the persistent, chromium-centered radicals $\{\eta^5\text{-}C_5H_5Cr(CO)_2L\}$ (L = CO, PMe_3, PMe_2Ph, $PMePh_2$, PPh_3) and $\{\eta^5\text{-}C_5Me_5Cr(CO)_3\}$ are reported. It is found that all undergo nearly reversible, 1-electron reductions to the corresponding anions, the relative ease of reduction correlating well with electron-donating abilities of the ligands, as indicated by observed values of ν_{CO}. At suitable combinations of low temperature and fast scan rates, exchange between the monomeric $\{\eta^5\text{-}C_5H_5Cr(CO)_3\}$ and its dimer, $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$, becomes sufficiently slow relative to the time scale of the cyclic voltammetric experiment that reduction of the dimer, the predominant species in solution, is observed.

As part of growing interest in the chemistry of 17-electron organometallic compounds,[1] it has recently been shown that the metal–metal-bonded, 18-electron compounds $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$ and $[\eta^5\text{-}C_5Me_5Cr(CO)_3]_2$ partially dissociate in solution to form the corresponding 17-electron, radical species, $\{\eta^5\text{-}C_5H_5Cr(CO)_3\}$ and $\{\eta^5\text{-}C_5Me_5Cr(CO)_3\}$, respectively.[2] The two monomers are labile and react with a variety of tertiary phosphines L to form substituted 17-electron compounds of the types $\{\eta^5\text{-}C_5H_5Cr(CO)_2L\}$ and $\{\eta^5\text{-}C_5Me_5Cr(CO)_2L\}$, most of which are monomeric both in solution and in the solid state.[3] We have been investigating the physical and chemical properties of $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$, $[\eta^5\text{-}C_5Me_5Cr(CO)_3]_2$, and their derivatives[2a,3] and have recently reported a detailed investigation of the X-ray structures of two substituted radicals, $\{\eta^5\text{-}C_5H_5Cr(CO)_2(PPh_3)\}$ and $\{\eta^5\text{-}C_5Me_5Cr(CO)_2(PMe_3)\}$, and of the electronic structures of both the tricarbonyl and of the substituted dicarbonyl radical species, as indicated by single-crystal EPR studies and LCAO-HFS calculations.[4]

In order to gain further information concerning the electronic structures of this fascinating series of compounds, we have now also carried out a cyclic voltammetric study of the compounds $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$, $[\eta^5\text{-}C_5Me_5Cr(CO)_3]_2$, and $\{\eta^5\text{-}C_5H_5Cr(CO)_2L\}$ (L = PMe_3, PMe_2Ph, $PMePh_2$, PPh_3) and report herein our results. Although electrochemical applications to organometallic chemistry are numerous,[5] previous electrochemical investigations of this system have been limited to a brief examination of $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$, for which it was con-

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