from the Johnson Matthey Research Centre. The cyclohexyl compounds were synthesized following published methods.[48]

Note Added in Proof. Since this manuscript was prepared, further work has been carried out (Molloy, K. C.; Tagliavini, G.; Ganis, P.; Furlani, D. *Inorg. Chim. Acta*, in press) on the solid-state structure of dicyclohexyltin dichloride, and the conclusions regarding tin coordination presented here were reinforced. The solid-state ^{119}Sn NMR spectra of five compounds, including Ph_3SnCl and Et_2SnCl_2, have been reported (Komoroski, R. A.; Parker, R. G.; Mazany, A. M.; Early, T. A. *J. Magn. Reson.* 1987, *73*, 389). The effects of residual dipolar coupling to chlorine are mentioned but not explained in detail. The isotropic chemical shifts appear to have been incorrectly reported (loc. cit. Table I).

Acknowledgment. The Deutsche Forschungsgemeinschaft is thanked for its support (of A.S.). We are grateful to P. Reams for the early work on Ph_3SnCl and to D. C. Apperley for the high-field spectrum of the same compound. We thank B. Wrackmeyer and the Johnson Matthey Research Centre for gifts of compounds.

Registry No. II, 639-58-7; III, 3151-41-5; IV, 3091-32-5; V, 3023-92-5; VI, 753-73-1; VII, 866-55-7; VIII, 683-18-1; IX, 3002-01-5; X, 3342-69-6; XI, 2954-94-1; XII, 2767-47-7; c-Hex_3SnOH, 13121-70-5; $(PhCH_2)_2Sn(C{\equiv}CPh)_2$, 111113-25-8.

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[48] Krause, E.; Pohland, R. *Ber. Dtsch. Chem. Ges.* 1924, *57*, 532.

Unidentate vs Bidentate Acyl Coordination: Reactions of High-Spin Iron(II) Alkyls with Carbon Monoxide and the Crystal Structure of the Bidentate Acyl $Fe(\eta^2\text{-}COC_6H_2Me_3)Br(CO)(dippe)$

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The carbonylation of the 14-electron high-spin iron(II) dialkyls FeR_2(dippe), dippe = 1,2-bis(diisopropylphosphino)ethane, leads to formation of the zerovalent iron carbonyl $Fe(CO)_3$(dippe) (1) and, for R = CH_2CMe_3, 2,2,6,6-tetramethyl-4-heptanone. When monoalkyl derivatives FeRX(dippe) are carbonylated, acyl-containing species are formed, and products containing unidentate or bidentate acyls have been isolated depending on the CO pressure and the identity of the alkyl group. Thus, when the carbonylation of $Fe(CH_2CMe_3)X$(dippe) is caried out by using approximately 2 equiv of CO, $Fe(\eta^2\text{-}COCH_2CMe_3)X(CO)$(dippe), **2a** (X = Br) and **2b** (X = Cl), are formed. The products **2a** and **2b** contain a bidentate acyl (ν_{COR} = 1591 and 1596 cm^{-1}, respectively) and only one terminal carbonyl ligand. Reaction of $Fe(CH_2CMe_3)X$(dippe) with excess CO at 3 atm gives $Fe(\eta^1\text{-}COCH_2CMe_3)X(CO)_2$(dippe), **4a** (X = Br) and **4b** (X = Cl), each of which contains a unidentate acyl (ν_{COR} = 1634 and 1630 cm^{-1}, respectively) and two carbonyl ligands. The major isomer formed in the latter reaction has been determined by ^{13}C and ^{31}P NMR spectroscopy to possess mutually trans acyl and halide ligands while the minor isomer has mutually trans carbonyl and halide ligands. Carbonylation of the iron(II) mesityl $Fe(C_6H_2Me_3)Br$(dippe) gives only the bidentate acyl product $Fe(\eta^2\text{-}COC_6H_2Me_3)Br(CO)$(dippe) (**3**) even with excess CO. The infrared absorption at 1525 cm^{-1} for the bidentate mesityl acyl is much lower in frequency than for the bidentate neopentyl acyls due to conjugation with the aromatic ring. Of the five isomers possible for this stoichiometry, **3** adopts a structure in which the carbonyl ligand is trans to the oxygen atom of the acyl group, as shown by ^{13}C and ^{31}P NMR data. This is confirmed by the X-ray crystal structure of **3**, which shows that the Fe center is six-coordinate and that the acyl group is indeed bidentate, with Fe–C_{acyl} = 1.85 (1) Å and Fe–O_{acyl} = 1.99 (1) Å. Compound **3** crystallizes in the monoclinic space group $P2_1/n$ with cell dimensions a = 10.470 (10) Å, b = 17.659 (16) Å, c = 15.259 (18) Å, β = 100.34 (8)°, V = 2775 (5) Å^3, Z = 4, R_F = 8.2%, and R_{wF} = 8.1% for 1969 independent reflections. A review of structural parameters for bidentate acyls of transition metals is given, and a comparison of the bonding in **3** with other molecules reveals that the Fe–O distance is unusually short as a result of steric "compression" from one of the ortho methyl groups of the mesityl substituent.

Introduction

Unsaturated species are the key intermediates in virtually all chemical reactions and catalytic processes involving transition-metal complexes. We have recently reported the synthesis and characterization of a series of tetrahedral, 14-electron organoiron compounds of stoichiometry FeR_2(dippe) and FeRX(dippe), where dippe is 1,2-bis(diisopropylphosphino)ethane and R is a β-stabilized alkyl.[1] The steric bulk of the dippe ligand allows the isolation of these unusual high-spin organoiron compounds in contrast to other phosphines such as PMe_3 or dmpe that invariably form octahedral, low-spin iron(II) species. We now describe the reactions of the highly coordinately unsaturated complexes FeR_2(dippe) and FeRX(dippe) with carbon monoxide to yield ketones and iron acyls as insertion products.

Most of the acyl complexes in the literature adopt unidentate coordination geometries,[2,3] whereas the first

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[1] Hermes, A. R.; Girolami, G. S. *Organometallics* 1987, *6*, 763-768.

[2] Wojcicki, A. *Adv. Organomet. Chem.* 1973, *11* 8-145.

bidentate acyl group was not definitively established until 1976;[4] earlier reports[5] of bidentate bonding modes have proven erroneous.[6] Bidentate acyls may be kinetically important species in the C–O bond cleavage step of Fischer–Tropsch catalysis: it has been suggested recently that they can cleave *directly* to give a metal carbyne and a metal oxo species. Such a rearrangement has been observed to occur on a metal cluster framework[7] and provides an alternative to the usual assumption that reduction to a hydroxyalkyl species occurs prior to C–O bond scission.[8-10] Of particular interest in the iron system described here is the isolation of both unidentate and bidentate acyl groups depending on the CO pressure and the identity of the alkyl group. Furthermore, we have determined the X-ray crystal structure of one of the bidentate iron acyl complexes, and a comparison of its geometry with other bidentate acyls in the literature reveals that the Fe–O interaction is unusually strong. The chemical factors that promote bidentate acyl bonding modes in this system may therefore be relevant to understanding the mechanism of CO bond scission in Fischer–Tropsch catalysis.

Results

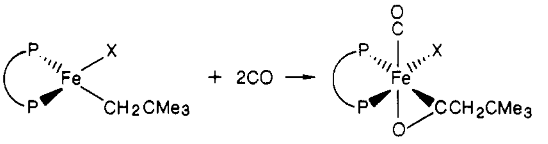
Reaction of 14-Electron Iron(II) Alkyls with Carbon Monoxide. Carbonylation of either the neopentyl or (trimethylsilyl)methyl FeR_2(dippe) species[1] in toluene at 3 atm rapidly results in a yellow solution from which the zerovalent tricarbonyl complex $Fe(CO)_3$(dippe) (**1**) may be isolated. This diamagnetic molecule exhibits ^1H and ^{31}P

$$FeR_2(\text{dippe}) + 4CO \rightarrow \underset{\mathbf{1}}{Fe(CO)_3(\text{dippe})} + R_2CO$$

NMR spectra consistent with a fluxional trigonal-bipyramidal structure, and its IR spectrum shows ν_{CO} absorptions at 1968, 1890, and 1872 cm^{-1} that are similar to other $Fe(CO)_3(PR_3)_2$ species.[11] Analysis of the organic products from the carbonylation of $Fe(CH_2CMe_3)_2$(dippe) by GC/MS and ^1H NMR revealed the exclusive presence of dineopentyl ketone (2,2,6,6-tetramethyl-4-heptanone). Ketone formation upon carbonylation of a transition-metal alkyl is a fairly common event.[12-19]

The reaction of $Fe(CH_2CMe_3)_2$(dippe) with CO proceeds through an orange intermediate that is apparent during the first few second of the carbonylation reaction. While we have been unable to stop the reaction at this stage or identify the species present spectroscopically, the assignment of this intermediate to an iron(II) acyl was tested by treating the monoalkyl derivatives FeRX(dippe) with CO.

Bidentate Acyl Complexes. Carbonylation of the 14-electron monoalkyl species FeRX(dippe) leads to diamagnetic products in which the alkyl groups have been retained in the coordination sphere as acyl ligands. Thus, carbonylation of $Fe(CH_2CMe_3)Br$(dippe) using approximately 2 equiv of CO gives the bidentate acyl complex $Fe(\eta^2\text{-}COCH_2CMe_3)Br(CO)$(dippe) (**2a**). The infrared spectrum of this species contains a terminal carbonyl stretch at 1908 cm^{-1} and an acyl stretch at 1591 cm^{-1} that falls in the <1600 cm^{-1} region typical of nonaromatic η^2-acyls. The carbonylation of the analogous chlorocomplex gives the corresponding bidentate acyl $Fe(\eta^2\text{-}COCH_2CMe_3)Cl(CO)$(dippe) (**2b**) which exhibits terminal CO and bidentate acyl stretches at 1905 and 1596 cm^{-1}, respectively.



2a, X = Br
b, X = Cl

A compound of similar stoichiometry, $Fe(COC_6H_2Me_3)Br(CO)$(dippe) (**3**), is obtained upon carbonylation of the iron mesityl complex $Fe(C_6H_2Me_3)Br$(dippe). For the mesityl acyl compound, the terminal CO stretch occurs at 1910 cm^{-1}, while the acyl absorption appears at 1520 cm^{-1}. Unfortunately, the position of the latter band cannot be attributed unambiguously to a bidentate geometry since the characteristic IR regions for aromatic η^1-acyls and η^2-acyls overlap. For example, the benzoyl compound $CpFe(\eta^1\text{-}COPh)$(dppe), dppe = 1,2-bis(diphenylphosphino)ethane, clearly possesses a unidentate acyl as shown by X-ray crystallography; however, the acyl CO stretch is found at 1510 cm^{-1}.[20] This low frequency may be attributed to conjugation of the C–O bond with the aromatic ring and strong back donation from a relatively electron-rich metal center. In any case, the single terminal carbonyl stretching mode and the similarities in the NMR spectra (see below) of the neopentyl and mesityl acyl complexes leave no doubt that the acyl ligand in $Fe(COC_6H_2Me_3)Br(CO)$(dippe) adopts a bidentate configuration despite the ambiguity of the IR frequencies.

Given the stoichiometries of **2** and **3**, five isomers are possible. The $^{31}P\{^1H\}$ NMR spectra in all cases show the presence of only one isomer with two inequivalent phosphorus nuclei and a $^2J_{PP}$ coupling constant of ca. 20 Hz. The presence of one acyl and one terminal carbonyl in **2** and **3** is confirmed by the equal intensity resonances at δ 260 and 228 in the $^{13}C\{^1H\}$ NMR spectra of the ^{13}C-enriched compounds. The ^{13}CO-labeled compounds can also help to assign the relative arrangements of the ligands by an analysis of the magnitudes of the ^{13}C–^{13}C and ^{13}C–^{31}P coupling constants. The ^{13}C NMR spectra of the neopentyl and mesityl acyl complexes are in general very similar; however, the resonances of the former are not particularly well-resolved even at −70 °C. By contrast, the $^{13}C\{^1H\}$ NMR spectra of the mesityl acyl complexes are well-defined and ascribable to a four-spin system ABXY, where A, B = ^{31}P and X, Y = ^{13}C. Simulations of the spectra

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(3) Calderazzo, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 299–311.

(4) Fachinetti, G.; Floriani, C.; Marchetti, F.; Merlino, S. *J. Chem. Soc., Chem. Commun.* **1976**, 522–523.

(5) Hitch, R. R.; Gondal, S. K.; Sears, C. J. *J. Chem. Soc., Chem. Commun.* **1971**, 777–778.

(6) Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **1977**, *142*, C1–C6.

(7) Shapley, J. R.; Park, J. T.; Churchill, M. R.; Ziller, J. W.; Beanan, L. R. *J. Am. Chem. Soc.* **1984**, *106*, 1145–1146.

(8) Pichler, H.; Schultz, H. *Chem.-Ing.-Tech.* **1970**, *42*, 1162–1174.

(9) Henrici-Olivé, G.; Olivé, S. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 136–141.

(10) Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61–103.

(11) Manuel, T. A. *Inorg. Chem.* **1963**, *2*, 854–858.

(12) Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 5421–5422.

(13) Carmona-Guzman, E.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1978**, 1139–1143.

(14) Girolami, G. S.; Mainz, V. V.; Andersen, R. A.; Vollmer, S. H.; Day, V. W. *J. Am. Chem. Soc.* **1981**, *103*, 3953–3954.

(15) Chiu, K. W.; Jones, R. A.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1981**, 2088–2097.

(16) Klein, H.-F.; Karsch, H. H. *Chem. Ber.* **1976**, *109*, 1453–1464.

(17) Salt, J. E.; Girolami, G. S.; Wilkinson, G.; Motevalli, M.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1985**, 685–692.

(18) Evitt, E. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1980**, *102*, 7003–7011.

(19) Maruyama, K.; Ito, T.; Yamamoto, A. *Transition Met. Chem. (Weinheim, Ger.)* **1980**, *5*, 14–16.

(20) Felkin, H.; Meunier, B.; Pascard, C.; Prange, T. *J. Organomet. Chem.* **1977**, *135*, 361–372.

Table I. Physical and Microanalytical Data for the New Iron Carbonyl and Acyl Complexes

compound	color	mp, °C	calcd C	calcd H	found C	found H
$Fe(CO)_3(dippe)$	lemon yellow	96	50.8	8.02	50.6	7.75
$Fe(COCH_2CMe_3)Br(CO)(dippe)$	red-orange	107–108	48.0	8.25	48.2	8.15[a]
$Fe(COCH_2CMe_3)Cl(CO)(dippe)$	red-orange	95–96	52.5	9.01	52.5	9.17[b]
$Fe(COC_6H_2Me_3)Br(CO)(dippe)$	red-orange	166	52.4	7.56	51.8	7.26[c]
$Fe(COCH_2CMe_3)Br(CO)_2(dippe)$	yellow-orange	133–135	47.8	7.83	47.2	7.40[d]
$Fe(COCH_2CMe_3)Cl(CO)_2(dippe)$	yellow-orange	130–132	51.9	8.52	52.4	8.67[e]

[a] Br: calcd, 15.2; found, 15.3. [b] Cl: calcd, 7.37; found, 7.53. [c] Br: calcd, 13.9; found, 13.8. [d] Br: calcd, 14.4; found, 15.6. [e] Cl: calcd, 6.97; found, 7.21.

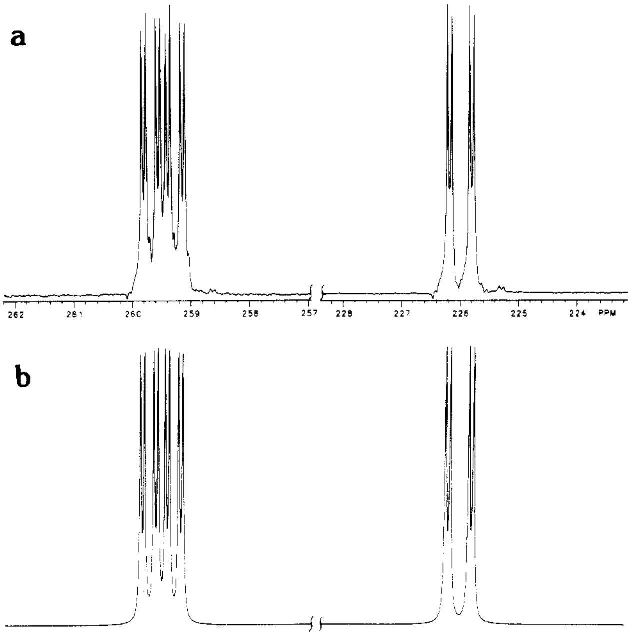

Figure 1. $^{13}C\{^1H\}$ NMR spectrum of $Fe(\eta^2\text{-}COC_6H_2Me_3)Br(CO)(dippe)$ (**3**) enriched to 100% ^{13}C at the acyl and carbonyl carbons: (a) observed; (b) simulated.

Table II. Crystal Data for $Fe(\eta^2\text{-}COC_6H_2Me_3)Br(CO)(dippe)$ (25 °C)

space group: $P2_1/n$
a = 10.470 (10) Å
b = 17.659 (16) Å
c = 15.259 (18) Å
β = 100.34 (8)°
$\alpha = \gamma$ = 90°
V = 2775 (5) Å^3
Z = 4
mol wt = 573.32
d_{calcd} = 1.372 g/cm^3
μ_{calcd} = 21.00 cm^{-1}
size = 0.2 × 0.4 × 0.4 mm
diffractometer: Syntex $P2_1$
radiation: Mo K$\bar{\alpha}$, $\bar{\lambda}$ = 0.71073 Å
monochromator: graphite crystal, monochromator angle = 6°
scan range, type, speed: $3.0 \leq 2\theta \leq 46.0$, $\omega/2\theta$, 3–20° min^{-1}
rflctns: 4479, 3887 unique, 1969 with $I > 2.58\sigma(I)$
internal consistency: R_i = 5.3%
R_F = 8.2%
R_{wF} = 8.1%
variables = 281
p factor = 0.03

Table III. Selected Bond Distances (Å) and Angles (deg) in $Fe(\eta^2\text{-}COC_6H_2Me_3)Br(CO)(dippe)$

Bond Distances			
Fe-P1	2.229 (4)	Fe-Br	2.513 (3)
Fe-P2	2.300 (4)	C1-O1	1.18 (2)
Fe-C1	1.70 (2)	C2-O2	1.28 (2)
Fe-C2	1.85 (1)	C2-C3	1.49 (2)
Fe-O2	1.99 (1)	C18-C19	1.56 (2)
Bond Angles			
Fe-C1-O1	178 (1)	P2-Fe-C1	102.1 (5)
Fe-C2-O2	76.4 (7)	P2-Fe-C2	144.8 (5)
Fe-C2-C3	162 (1)	P2-Fe-O2	106.3 (3)
Fe-O2-C2	64.9 (7)	P2-Fe-Br	91.5 (1)
O2-C2-C3	121 (1)	C1-Fe-C2	112.6 (7)
P1-Fe-P2	86.7 (1)	C1-Fe-O2	150.9 (6)
P1-Fe-C1	95.0 (5)	C1-Fe-Br	85.1 (5)
P1-Fe-C2	95.6 (4)	C2-Fe-O2	38.6 (5)
P1-Fe-O2	93.3 (3)	C2-Fe-Br	86.1 (4)
P1-Fe-Br	178.1 (1)	O2-Fe-Br	87.5 (3)

revealed the magnitudes of all six coupling constants (see Figure 1). The $^2J_{CC}$ coupling constant between the acyl and carbonyl groups is 5.5 Hz, which implies that these ligands are mutually cis,[21,22] since trans $^2J_{CC}$ coupling constants are typically an order of magnitude larger at 30–40 Hz.[23] This observation rules out one of the five possible isomers.

In theory, the magnitudes of the $^2J_{CP}$ coupling constants should reveal whether the CO and COR groups are cis or trans to the phosphine ligand since for octahedral iron compounds they fall into ranges of 0–25 and 25–50 Hz, respectively.[22,24,25] The terminal carbonyl group is coupled to the two inequivalent phosphorus nuclei with relatively small coupling constants of 0 and 17.7 Hz and thus is most reasonably assigned a position cis to both; this assignment would rule out two of the remaining four geometric isomers, leaving as the only possibilities the structures where the carbonyl group is trans to the bromide ligand or the oxygen atom of the bidentate acyl. Accordingly, the carbon atom of the acyl ligand would be trans to one end of the phosphine ligand and cis to the other. However, the observed $^2J_{PC}$ coupling constants for the acyl carbon are 27.3 and 32.5 Hz, and these cannot be assigned unambiguously since there can be at most only one trans coupling. We conclude that perhaps an octahedral coordination environment is not the best description of the structure: the interligand angles may be quite severely perturbed due to the small bite (C–Fe–O angle) of the bidentate acyl group, so that the coupling constants cannot be divided into cis (small J) and trans (large J) interactions. In order to determine the exact coordination polyhedron and to determine unambiguously the identity of the isomer formed, a crystal structure determination of **3** has been carried out. Because of the spectroscopic (IR and NMR) similarities of **2** and **3**, the bidentate neopentyl and mesityl acyl complexes are presumed to have similar structures.

Structure of $Fe(\eta^2\text{-}COC_6H_2Me_3)Br(CO)(dippe)$. Single crystals of **3** were obtained by cooling saturated tetrahydrofuran solutions to −20 °C. Crystal data are given in Table I, while final atomic coordinates and anisotropic thermal parameters are given with standard deviations in Tables II and III. Selected bond lengths and angles are presented with standard deviations in Table IV.

The structural analysis shows that crystals of **3** are composed of discrete molecules of $Fe(\eta^2\text{-}COC_6H_2Me_3)Br$-

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[21] Aime, S.; Osella, D. *J. Chem. Soc., Chem. Commun.* **1981**, 300–302.

[22] Cardaci, G.; Reichback, G.; Bellachioma, G. *Inorg. Chem.* **1984**, *23*, 2936–2940.

[23] Tachikawa, M.; Richter, S. I.; Shapley, J. R. *J. Organomet. Chem.* **1977**, *128*, C9–C14.

[24] Todd, L. S.; Wilkinson, J. R. *J. Organomet. Chem.* **1974**, *77*, 1–25.

[25] Jablonski, C. R.; Wang, Y-P. *Inorg. Chem.* **1982**, *21*, 4037–4044.

Table IV. Final Atomic Coordinates for $Fe(\eta^2\text{-}COC_6H_2Me_3)Br(CO)(dippe)$

	x/a	*y/b*	*z/c*
Br	0.3873 (2)	0.2489 (1)	0.6679 (1)
Fe	0.3028 (2)	0.1269 (1)	0.7203 (1)
P1	0.2342 (3)	0.0171 (2)	0.7670 (3)
P2	0.5093 (3)	0.0782 (2)	0.7561 (3)
O1	0.234 (1)	0.0938 (7)	0.5336 (8)
O2	0.2707 (9)	0.1828 (5)	0.8275 (6)
C1	0.262 (1)	0.1057 (9)	0.610 (1)
C2	0.178 (1)	0.1859 (7)	0.760 (1)
C3	0.056 (1)	0.2278 (8)	0.765 (1)
C4	0.021 (1)	0.2464 (9)	0.847 (1)
C5	−0.097 (2)	0.2870 (9)	0.843 (2)
C6	−0.176 (2)	0.307 (1)	0.764 (3)
C7	−0.138 (2)	0.283 (1)	0.690 (2)
C8	−0.022 (2)	0.2447 (9)	0.684 (1)
C9	0.099 (2)	0.2347 (10)	0.936 (1)
C10	−0.299 (2)	0.3502 (10)	0.767 (2)
C11	0.011 (2)	0.2274 (10)	0.597 (1)
C12	0.165 (1)	0.0248 (8)	0.870 (1)
C13	0.272 (2)	0.0461 (9)	0.9515 (10)
C14	0.091 (1)	−0.0435 (9)	0.894 (1)
C15	0.109 (1)	−0.0413 (8)	0.6925 (10)
C16	−0.012 (1)	0.0076 (9)	0.662 (1)
C17	0.154 (2)	−0.0770 (10)	0.615 (1)
C18	0.369 (1)	−0.0507 (8)	0.7965 (9)
C19	0.502 (1)	−0.0086 (8)	0.825 (1)
C20	0.631 (1)	0.1396 (8)	0.824 (1)
C21	0.584 (1)	0.1723 (10)	0.904 (1)
C22	0.764 (1)	0.0994 (9)	0.852 (1)
C23	0.600 (2)	0.044 (1)	0.668 (1)
C24	0.524 (2)	−0.022 (1)	0.615 (1)
C25	0.627 (2)	0.1082 (10)	0.611 (1)

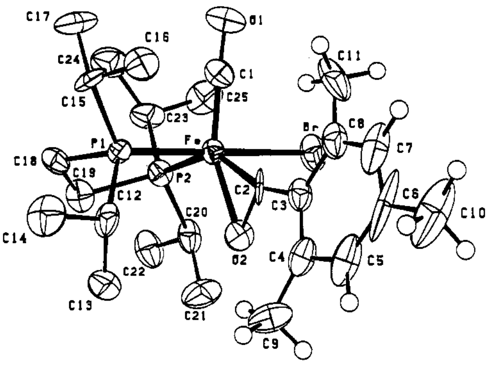


Figure 2. ORTEP view of the molecular structure of $Fe(\eta^2\text{-}COC_6H_2Me_3)Br(CO)(dippe)$ (**3**).

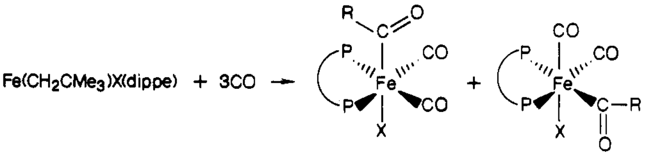
(CO)(dippe); a perspective view of the molecule is shown in Figure 2. The iron center is six-coordinate with a severely distorted octahedral coordination geometry. Alternatively, the geometry may be described in terms of a five-coordinate trigonal-bipyramidal structure with the C2–O2 bond of the bidentate acyl considered to occupy one coordination site. The axial positions are defined by P1 and Br1 with the P1–Fe–Br1 angle being 178°, while the trigonal plane contains P1, C1, and the C2–O2 bond. The Fe–P bond lengths of 2.229 (4) and 2.300 (4) Å are in the 2.24–2.30 Å range reported for low-spin Fe(II) compounds.[1] The P1–Fe–P2 angle of 86.7 (1)° is normal and reflects the chelating nature of the phosphine ligand. The "trans" C2–Fe–P2 angle of 144.8 (5)° explains why the $^2J_{CP}$ coupling constants could not be unambiguously ascribed to cis or trans couplings.

The structure clearly reveals a bidentate coordination for the acyl group, with Fe–C and Fe–O bond lengths of 1.85 (1) and 1.99 (1) Å, respectively. The Fe⋯O contacts in compounds containing unidentate acyls are significantly longer; for example in $CpFe(\eta^1\text{-}COPh)(dppe)$ (**5**),[20] $CpFe(\eta^1\text{-}COPh)(CO)(PPh_3)$ (**6**),[26] $(C_5H_3MePh)Fe(\eta^1\text{-}COMe)(PPh_3)(CO)$ (**7**),[27] $CpFe(\eta^1\text{-}COCHPMe_3)(CO)_2$ (**8**),[28] and $(HBpz_3)Fe(\eta^1\text{-}COMe)(CO)_2$ (**9**),[29] the Fe⋯O contacts are all ca. 2.83 Å, clearly indicating that no significant Fe–O interactions are present. The $Fe\text{–}C_{acyl}$ distance in **3** is also somewhat shorter than the Fe–C distances in **5**–**9** of 1.93 (2)–2.04 (1) Å. Here and in bidentate acyl compounds in general, the shortened Fe–C distance in **3** reflects some double-bond or carbene-like character.

The mesityl ring adopts a conformation that allows substantial conjugation between the aromatic π system and the $\overline{\mathrm{Fe{-}O{-}C}}$ unit: the dihedral angle between the FeOC plane and the ring plane is 17°. Although unidentate aromatic acyls such as **5** do not generally exhibit such strong conjugation (dihedral angle of ca. 60°),[20] it is the rule for all known bidentate aromatic acyls (see Table VI). One consequence of the conjugation between the aromatic ring and the FeOC unit in **3** is that the ortho methyl group C9 is positioned very close to the acyl oxygen atom O2.

Overall, the structure of **3** is most closely related to the isopropyl acyl analogue $Fe(\eta^2\text{-}CO\text{-}i\text{-}Pr)I(CO)(PEt_3)_2$ (see below), except that in this molecule the unidentate phosphines are trans to one another rather than cis. More importantly, however, the angles and distances around the bidentate acyl are significantly different in the two compounds, and a fuller discussion of the structure of **3** compared with those of other bidentate acyls will be given below.

Unidentate Acyl Complexes. Excess carbon monoxide converts the high-spin iron alkyls in some cases to unidentate acyl complexes that contain an additional equivalent of incorporated CO. Thus, reaction of $Fe(CH_2CMe_3)Br(dippe)$ with carbon monoxide at 3 atm and 25 °C gives $Fe(\eta^1\text{-}COCH_2CMe_3)Br(CO)_2(dippe)$, which possesses two terminal carbonyl groups (ν_{CO} = 2004 and 1959 cm^{-1}) and a unidentate acyl ligand (ν_{CO} = 1634 cm^{-1}).



4a, X = Br
b, X = Cl

5a, X = Br
b, X = Cl

The $^{31}P\{^1H\}$ NMR spectrum shows that two of the four possible isomers are present in solution in a ratio of 20:1. The major isomer has C_s symmetry as indicated by a singlet in the $^{31}P\{^1H\}$ NMR spectrum. The carbonylation of the chloro derivative $Fe(CH_2CMe_3)Cl(dippe)$ under the same conditions gives similar products.

In order to confirm the identity of the major isomer, the carbonylation was carried out by using ^{13}CO. The $^{13}C\{^1H\}$ NMR spectrum of the major isomer shows that the two terminal carbonyl groups are chemically equivalent. The $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra of the ^{13}C-enriched chloro derivative (Figure 3) are clearly indicative of an AA′XX′Y spin system (A = ^{31}P; X, Y = ^{13}C). Additionally, the dippe region of the spectrum shows resonances for *four* different methyl carbons, *two* different methine carbons, and *one* methylene carbon. The $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spin systems and the number of dippe carbon resonances ob-

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[26] Semion, V. A.; Struchkov, Y. T. *J. Struct. Chem.* (*Engl. Transl.*) **1969**, *10*, 563–569.

[27] Attig, T. G.; Teller, R. G.; Wu, S. M.; Bau, R.; Wojcicki, A. *J. Am. Chem. Soc.* **1979**, *101*, 619–628.

[28] Blau, H.; Malisch, W.; Voran, S.; Blank, K.; Krüger, C. *J. Organomet. Chem.* **1980**, *202*, C33–C38.

[29] Cotton, F. A.; Frenz, B. A.; Shaver, A. *Inorg. Chim.* Acta **1973**, *7*, 161–169.

Table V. Anisotropic Thermal Parameters for $Fe(\eta^2\text{-}COC_6H_2Me_3)Br(CO)(dippe)$

	U(11), *U*(iso)	*U*(22)	*U*(33)	*U*(23)	*U*(13)	*U*(12)
Br	0.062 (1)	0.054 (1)	0.095 (2)	0.023 (1)	0.008 (1)	−0.0111 (10)
Fe	0.037 (1)	0.037 (1)	0.045 (1)	0.004 (1)	0.0037 (10)	0.000 (1)
P1	0.042 (2)	0.033 (2)	0.041 (3)	−0.004 (2)	0.011 (2)	−0.003 (2)
P2	0.039 (2)	0.048 (3)	0.048 (3)	0.003 (2)	0.010 (2)	0.007 (2)
O1	0.088 (9)	0.11 (1)	0.042 (8)	−0.003 (7)	0.001 (7)	−0.004 (7)
O2	0.041 (6)	0.059 (7)	0.060 (7)	−0.003 (6)	−0.003 (6)	0.011 (5)
C1	0.048 (10)	0.07 (1)	0.05 (1)	0.010 (10)	0.015 (9)	−0.004 (8)
C2	0.030 (9)	0.008 (7)	0.09 (1)	0.018 (8)	−0.005 (8)	0.001 (6)
C3	0.038 (9)	0.04 (1)	0.07 (1)	0.008 (9)	−0.004 (10)	0.004 (7)
C4	0.05 (1)	0.038 (10)	0.09 (2)	−0.00 (1)	0.02 (1)	−0.008 (9)
C5	0.05 (1)	0.04 (1)	0.16 (2)	−0.01 (1)	0.05 (1)	0.006 (10)
C6	0.03 (1)	0.02 (1)	0.34 (5)	−0.03 (2)	−0.01 (2)	0.004 (9)
C7	0.05 (1)	0.04 (1)	0.19 (3)	−0.01 (1)	−0.03 (2)	0.00 (1)
C8	0.06 (1)	0.04 (1)	0.09 (2)	0.01 (1)	0.00 (1)	−0.008 (10)
C9	0.08 (1)	0.10 (2)	0.07 (1)	−0.04 (1)	0.03 (1)	0.00 (1)
C10	0.04 (1)	0.07 (1)	0.32 (3)	−0.06 (2)	−0.01 (2)	0.01 (1)
C11	0.07 (1)	0.10 (2)	0.10 (2)	0.06 (1)	−0.04 (1)	−0.01 (1)
C12	0.047 (9)	0.032 (9)	0.08 (1)	0.002 (9)	−0.008 (9)	−0.013 (8)
C13	0.09 (1)	0.07 (1)	0.05 (1)	0.004 (9)	0.02 (1)	−0.01 (1)
C14	0.06 (1)	0.08 (1)	0.10 (2)	−0.00 (1)	0.01 (1)	−0.03 (1)
C15	0.07 (1)	0.043 (9)	0.06 (1)	−0.034 (9)	0.014 (9)	−0.021 (9)
C16	0.047 (10)	0.07 (1)	0.07 (1)	0.002 (10)	−0.006 (9)	−0.018 (9)
C17	0.10 (1)	0.10 (2)	0.05 (1)	−0.04 (1)	−0.00 (1)	−0.01 (1)
C18	0.06 (1)	0.06 (1)	0.039 (10)	0.011 (8)	0.019 (8)	−0.003 (9)
C19	0.054 (10)	0.06 (1)	0.07 (1)	0.011 (9)	0.025 (9)	0.007 (9)
C20	0.035 (9)	0.048 (10)	0.08 (1)	0.016 (10)	−0.005 (9)	0.003 (8)
C21	0.06 (1)	0.10 (2)	0.08 (1)	−0.04 (1)	−0.02 (1)	−0.01 (1)
C22	0.06 (1)	0.08 (1)	0.09 (1)	0.03 (1)	0.00 (1)	0.002 (10)
C23	0.07 (1)	0.09 (1)	0.05 (1)	−0.01 (1)	0.027 (10)	0.01 (1)
C24	0.08 (1)	0.11 (2)	0.07 (1)	−0.01 (1)	0.02 (1)	0.02 (1)
C25	0.08 (1)	0.09 (2)	0.09 (1)	−0.02 (1)	0.05 (1)	−0.01 (1)
H	0.11 (1)					

Table VI. Summary of Spectroscopic and Crystallographic Data for Bidentate Acyls of Transition Metals[a]

compd	ν_{cor}	$\delta(^{13}C)$	M–C	M–O	C–O	Δ(MO–MC)	ref
$(C_5Me_5)_2Th(COCH_2CMe_3)Cl$	1469	360	2.44 (2)	2.37 (2)	1.18 (3)	−0.07	35
$Cp_3U(COCHPMePh_2)$			2.37 (2)	2.27 (1)	1.27 (3)	−0.10	36
$Cp_2Ti(COMe)Cl$	1620		2.07 (2)	2.19 (1)	1.18 (2)	0.12	37
$Cp_2Zr(COMe)Me$	1545		2.197 (6)	2.290 (4)	1.211 (8)	0.093	38
$Cp_2Zr(COMe)[OCMo(CO)_2Cp]$	1590	316	2.186 (4)	2.249 (3)	1.241 (5)	0.063	39
$V(COC_3H_2Ph_3)(CO)_3(arphos)$	1505		2.01 (1)	2.24 (1)	1.19 (2)	0.23	40
$[HBpz_3]Mo(COMe)(CO)_2$	1570	265	2.022 (9)	2.224 (6)	1.22 (1)	0.202	41
$[HBpz_3]Mo(COPh)(CO)_2$		254	2.021 (5)	2.189 (3)	1.224 (6)	0.168	41
$[HB(3,5\text{-}Me_2pz)_3]Mo(CO\text{-}c\text{-}Hx)(CO)_2$			1.996 (9)	2.291 (6)	1.26 (1)	0.295	42
$[HB(3,5\text{-}Me_2pz)_3]Mo(CO\text{-}p\text{-}Tol)(CO)_2$			2.005 (2)	2.287 (2)	1.245 (3)	0.282	42
$[Mo(COCH_2SiMe_3)Cl(CO)(PMe_3)]_2$	1585		2.023 (3)	2.292 (2)	1.225 (4)	0.269	43
$[W(COCH_2SiMe_3)Cl(CO)(PMe_3)]_2$	1530		2.029 (7)	2.289 (5)	1.233 (9)	0.260	44
$CpW(COEt)Cl_2(CO)$			1.999 (8)	2.167 (6)	1.246 (9)	0.168	45
$Fe(CO\text{-}i\text{-}Pr)I(CO)(PEt_3)_2$	1586	286	1.80 (2)	2.19 (2)	1.24 (2)	0.39	46
$Fe(COC_6H_2Me_3)Br(CO)(dippe)$	1525	260	1.85 (1)	1.99 (1)	1.28 (2)	0.14	this work
$Ru(COMe)I(CO)(PPh_3)_2$	1599		1.88 (3)	2.47 (2)	1.33 (4)	0.59	47
$Ru(CO\text{-}p\text{-}Tol)I(CO)(PPh_3)_2$	1550		1.92 (1)	2.36 (1)	1.21 (2)	0.44	47
$Os(CO\text{-}o\text{-}Tol)Cl(CH_2)(PPh_3)_2$	1506		1.86 (1)	2.423 (9)	1.22 (1)	0.56	48

[a] ν_{COR} in cm^{-1}; $\delta(^{13}C)$ in ppm from TMS; distances in Å.

served are consistent only with the isomer of C_s symmetry, 4.

The NMR spectra of the minor isomer (Figure 3) are interpretable in terms of an ABXYZ spin system (A, B = ^{31}P; X, Y, Z = ^{13}C). The presence of a large J_{PC} coupling of 49.8 Hz with one of the carbonyls, and a second larger J_{PC} coupling of 43.1 Hz with the acyl ligand establishes 5 as the structure of the minor isomer. The major and minor isomers are related by interchanging the acyl ligand and one of the carbonyl groups. The ability to distinguish cis from trans coupling constants in 4 and 5 suggests that these compounds, unlike the bidentate acyl complexes, adopt regular octahedral structures.

Interestingly, carbonylation of the 14-electron mesityl complex $Fe(C_6H_2Me_3)Br(dippe)$ gives only the bidentate acyl 3 even with excess CO. No evidence of a unidentate mesityl acyl product was noted under conditions (3 atm, 12 h) that rapidly lead to unidentate neopentyl acyls.

Discussion

High-spin organometallic complexes are expected to exhibit less covalent and more ionic bonding between the metal and the ligands, relative to their low-spin analogues. Comparisons of the chemistry of the high-spin complexes $FeR_2(dippe)$ with that of alkyls of early transition elements, such as zirconium, hafnium, and the f-block elements, may therefore be instructive. Specifically, alkyl derivatives of these electropositive metals are known to react with carbon monoxide to give acyls possessing significant carbene-like character that can lead in some cases to hydrogen migration and C–C coupling reactions.[30-32]

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(30) Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 2716–2724.

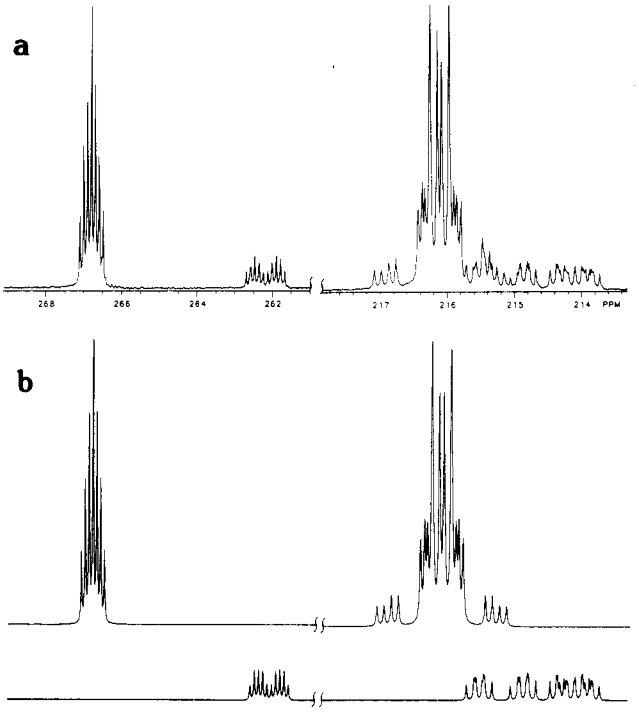

Figure 3. $^{13}C\{^1H\}$ NMR spectrum of $Fe(\eta^1\text{-}COCH_2CMe_3)Cl(CO)_2(dippe)$, enriched to 100% ^{13}C at the acyl and carbonyl carbons: (a) observed; (b) simulated spectrum showing the components due to the major isomer **4b** (upper trace) and the minor isomer **5b** (lower trace).

The carbonylation of the $FeR_2(dippe)$ species to give ketones and $Fe(CO)_3(dippe)$ most likely proceeds via acyl intermediates,[33] which may be isolated by carbonylation of the FeRX(dippe) monoalkyl complexes.[34] Interestingly, no evidence of carbene-like reactivity of the acyl groups has been noted in this system. These results indicate that conversion from a high-spin to a low-spin configuration probably occurs early in the carbonylation sequence. Not surprisingly, after becoming low-spin, the behavior of the iron acyls closely resembles that of other low-spin organometallic complexes.

Structural Comparisons of Bidentate Acyl Complexes. Structurally characterized compounds containing bidentate acyls have been reported for metals of groups 4, 5, 6, 8 and the actinide series.[35-48] The two geometric parameters that best characterize the nature of the M–C–O interaction are the C–O bond distance and the difference in the M–O and M–C contacts. A summary of crystallographic data for bidentate acyl complexes is given in Table VI along with the spectroscopic parameters ν_{COR} and $\delta(^{13}C)$ where these values are available.

The C–O distances vary from 1.18 (2) to 1.33 (4) Å, but the relatively large uncertainties in this bond length do not allow meaningful comparisons to be made from compound to compound. In general, the C–O distance for a bidentate acyl may be taken at 1.23 ± 0.02 Å, with only the less accurately determined structures (largest estimated standard deviations) having distances that fall significantly outside of this range.

Much more informative than the CO bond length is the difference in the metal–oxygen and metal–carbon distances, Δ(MO–MC). As shown in Table VI, the "oxophilic" actinide and group 4 metals have roughly identical M–O and M–C contacts; in fact for the actinide complexes the M–O distance is slightly *shorter* than the M–C distance. The Δ(MO–MC) parameter increases roughly with increasing electronegativity[49] (decreasing oxophilicity) of M: actinides ($\chi = 1.3$, $\Delta = -0.1$ Å), group 4 ($\chi = 1.5$, $\Delta = +0.1$ Å), groups 5 and 6 ($\chi = 1.6$, $\Delta = +0.25$ Å), group 8 ($\chi = 1.8$, $\Delta = +0.4$ to $+0.6$ Å). Essentially all the variation in Δ may be attributed to differences in the strength of the metal–oxygen interaction, since the metal–carbon distances are essentially constant for different compounds of the same metal; in fact the M–C distances in all of the bidentate acyls may be predicted fairly accurately by adding 1.25 Å to the ionic metal radii tabulated by Shannon.[50]

Interestingly, the bidentate acyl $Fe(\eta^2\text{-}COC_6H_2Me_3)Br(CO)(dippe)$ (**3**) described above does not follow this general trend. The difference between the metal–oxygen and metal–carbon distances of only 0.14 Å is more typical of group 4 rather than group 8 acyls. A comparison of **3** with the other iron acyl in Table VI, $Fe(\eta^2\text{-}CO\text{-}i\text{-}Pr)I(CO)(PEt_3)_2$,[46] shows that the metal–carbon distance is essentially unchanged but the Fe–O distance in **3** is some 0.25 Å shorter than expected from the correlation between χ and Δ. In fact, the Fe–O distance of 1.99 (1) Å is the shortest such contact observed for *any* bidentate acyl. At first glance it might appear that the iron center in **3** must be engaging in greater π back-donation into the acyl π* orbital, but this is not consistent with the ^{13}C NMR chemical shifts and, furthermore, there is no reason to expect that **3** and $Fe(CO\text{-}i\text{-}Pr)I(CO)(PEt_3)_2$ should differ significantly in an electronic sense.

The most reasonable explanation for the unusually short Fe–O distance in **3** is steric in nature rather than electronic. The conjugation of the aromatic mesityl ring with the carbonyl functionality places the ortho methyl groups in roughly the same plane as the $\overline{Fe\text{–}O\text{–}C}$ unit. In particular, this forces the ortho carbon atom C9 to be only 2.80 Å from O2, and this contact is well inside the 3.40 Å sum of the

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[31] Sonnenberger, D. C.; Mintz, E. A.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 3484–3491.

[32] Moloy, K. G.; Fagan, P. J.; Manriquez, J. M.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 56–67.

[33] For mechanistic studies of CO insertion into Fe–C bonds in a similar system, see: Reichenbach, G.; Bellachioma, G. *J. Chem. Soc., Dalton Trans.* **1987**, 519–521 and references therein.

[34] Similar differences in CO reactivity have been observed between Cp_2ZrR_2 and Cp_2ZrRCl compounds: Schwartz, J.; Labinger, J. A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 333–340.

[35] Fagan, P. J.; Manriquez, J. M.; Marks, T. J.; Day, V. W.; Vollmer, S. H.; Day, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 5393–5396.

[36] Cramer, R. E.; Maynard, R. B.; Paw, J. C.; Gilje, J. W. *Organometallics* **1982**, *1*, 869–871.

[37] Fachinetti, G.; Floriani, C.; Stoeckli-Evans, H. *J. Chem. Soc., Dalton Trans.* **1977**, 2297–2302.

[38] Fachinetti, G.; Fochi, G.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1977**, 1946–1950.

[39] Marsella, J. A.; Huffman, J. C.; Caulton, K. G.; Longato, B.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 6360–6368.

[40] Franke, U.; Weiss, E. *J. Organomet. Chem.* **1979**, *165*, 329–340.

[41] Curtis, M. D.; Shiu, K.-B.; Butler, W. M. *Organometallics* **1983**, *2*, 1475–1477.

[42] Desmond T.; Lalor, F. J.; Ferguson, G.; Ruhl, B.; Parvez, M. *J. Chem. Soc., Chem. Commun.* **1983**, 55–56.

[43] Carmona-Guzman, E.; Wilkinson, G.; Rogers, R. D.; Hunter, W. E.; Zaworotko, M. J.; Atwood, J. L. *J. Chem. Soc., Dalton Trans.* **1980**, 229–234.

[44] Carmona, E.; Marin, J. M.; Poveda, M. L.; Sanchez, L.; Rogers, R. D.; Atwood, J. L. *J. Chem. Soc., Dalton Trans.* **1983**, 1003–1005.

[45] Kreissl, F. R.; Sieber, W. J.; Wolfgruber, M.; Riede, J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 640.

[46] Birk, R.; Berke, H.; Huttner, G.; Zsolnai, L. *J. Organomet. Chem.* **1986**, *309*, C13–C20.

[47] Roper, W. R.; Taylor, G. E.; Waters, J. M.; Wright, L. J. *J. Organomet. Chem.* **1979**, *182*, C46–C48.

[48] Bohle, D. S.; Clark, G. R.; Rickard, C. E. F.; Roper, W. R.; Shepard, W. E. B.; Wright, L. J. *J. Chem. Soc., Chem. Commun.* **1987**, 563–564.

[49] Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

[50] Shannon, R. D. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crytallogr.* **1976**, *32*, 751–767.

van der Waals radii for an oxygen atom and a methyl group.[49] In essence, O2 is close to the iron center because it must move away from the methyl group C9. This type of steric "compression" is not observed for any of the other bidentate acyls since they are considerably less crowded about the oxygen atom. Indeed, the acyl group in **3** contains by far the bulkiest substituent of all of the bidentate acyls that have been examined crystallographically.

We conclude that while the M–O distances in bidentate acyls are normally a function of the electronegativity of M, in certain cases steric effects can shorten the M–O distances by up to 0.25 Å.

Relative Stabilities of Unidentate and Bidentate Acyls. In the FeR_2(dippe) system described above, the neopentyl complexes are rapidly carbonylated to η^1-acyls via bidentate intermediates, whereas the mesityl complex stops at the η^2-acyl stage even with excess CO. The structural data for the mesityl acyl **3** provide a logical explanation of this behavior: the conjugation of the aromatic ring with the $\overline{\mathrm{Fe{-}O{-}C}}$ unit and the steric "compression" of the Fe–O bond in **3** makes the iron–oxygen interaction strong and prevents dissociation of the oxygen atom from the iron center. The carbonylation sequence in this case is thus stopped at the η^2-acyl stage.[51]

This observation reveals much about the specific factors that govern the interrelationship between unidentate and bidentate acyls. Certainly a deficiency of carbon monoxide will tend to favor a bidentate acyl while an excess will tend to favor a unidentate acyl with an additional equivalent of coordinated CO in the molecule. But apart from these broad thermodynamic considerations, it is clear that steric as well as electronic factors can influence the ease of the $\eta^2 \rightarrow \eta^1$ acyl rearrangement by affecting the strength of the metal–oxygen bond. These observations may be relevant to the C–O bond cleavage step in Fischer–Tropsch catalysis since they show one way in which the metal–oxygen interaction in a bidentate acyl can be strengthened, thereby promoting C–O bond scission.[7-10]

Experimental Section

All operations were carried out in vacuum or under argon. Solvents were distilled under nitrogen from sodium (toluene) or sodium–benzophenone (pentane, diethyl ether, tetrahydrofuran) immediately before use. 1,2-Bis(diisopropylphosphino)ethane was prepared via a literature route.[52] Labeled ^{13}CO (99% enriched) was obtained from Isotec, Inc. The iron dialkyl and monoalkyl complexes, FeR_2(dippe) and FeRBr(dippe), respectively, were prepared as described elsewhere.[1]

Microanalyses were performed by Mr. Josef Nemeth of the University of Illinois Microanalytical Laboratory. The IR spectra were recorded on a Perkin-Elmer 599B as Nujol mulls. The ^1H and ^{13}C NMR data were obtained on a General Electric QE-300 spectrometer at 300 MHz while the ^{31}P NMR data were obtained at 101.265 MHz on a locally constructed instrument. Chemical shifts are reported in δ units relative to TMS (^1H, ^{13}C) or 85% H_3PO_4 (^{31}P). Simulations of NMR spectra were performed using the program ITRCAL, written by Nicolet Technology Corp. The mass spectra were recorded on a VG 7070E instrument by the Mass Spectroscopy Laboratory of the University of Illinois. Melting points were measured on a Thomas-Hoover Unimelt apparatus in closed capillaries under argon.

1. Tricarbonyl[1,2-bis(diisopropylphosphino)ethane]iron(0). The neopentyl complex $Fe(CH_2CMe_3)_2$(dippe) (0.1 g, 0.22 mmol) was dissolved in toluene (20 mL) in a Fisher-Porter bottle, which was then pressurized to 3 atm with carbon monoxide. Within 10 min, the yellow solution turned orange and then back to yellow. The toluene was removed in vacuo, and the residue was extracted with pentane (20 mL). After the extract was filtered, concentrated to ca. 10 mL, and cooled to −20 °C, lemon yellow needles of $Fe(CO)_3$(dippe) were obtained. IR (cm^{-1}): 1968, 1890, 1872 (ν_{CO}). ^1H NMR (C_6D_6, 25 °C): δ 0.87 (dd, J_{PH} = 13.0, J_{HH} = 6.9 Hz, $CHMe_2$); 1.04 (dd, J_{PH} = 15.2, J_{HH} = 7.1 Hz, $CHMe_2$); 1.17 (d, J_{PH} = 12.4 Hz, PCH_2); 1.97 (m, $CHMe_2$). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): δ 120.2 (s). The same product may be obtained from the carbonylation of the (trimethylsilyl)methyl complex $Fe(CH_2SiMe_3)_2$(dippe).

In a similar fashion, the carbonylation of $Fe(CH_2CMe_3)_2$(dippe) was carried out by using 99% enriched ^{13}CO. $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ 18.3 (s, $CHMe_2$); 19.2 (s, $CHMe_2$); 23.4 ("t", $^1J_{PC} + {}^4J_{PC}$ = 41.0 Hz, PCH_2); 28.4 ("t", $^1J_{PC} + {}^4J_{PC}$ = 22.6 Hz, $CHMe_2$); 223.6 (t, J_{PC} = 6.7 Hz, CO).

In a separate experiment to identify the organic products, the reaction of $Fe(CH_2CMe_3)_2$(dippe) with CO was carried out in C_6D_6. After carbonylation under the same conditions as above, the solvent and volatile products were removed in vacuo and collected in a liquid-nitrogen trap. The only organic product observed under these conditions was dineopentyl ketone as identified by ^1H NMR and GC/MS. ^1H NMR (C_6D_6, 25 °C): δ 0.98 (s, CMe_3), 1.95 (s, CH_2); [lit. NMR ($CDCl_3$): δ 1.03, 2.29]. GC/MS (electron impact): M^+ 170 (32% of base peak). The fragmentation pattern was consistent with dineopentyl ketone.

2. Neopentylchloro[1,2-bis(diisopropylphosphino)ethane]iron(II). To a cold (−78 °C) suspension of $FeCl_2$(dippe) (1.20 g, 3.08 mmol) in diethyl ether (30 mL) was added dineopentylmagnesium[53] (6.2 mL of a 0.25 M solution in ether, 1.55 mmol). The solution turned yellow as the $FeCl_2$(dippe) dissolved. After being stirred for 2 h at −78 °C, the reaction solution was warmed to room temperature and stirred an additional 12 h. The ether was removed in vacuo, and the residue was extracted with pentane (100 mL). The extract was filtered and concentrated to ca. 50 mL. Cooling to −20 °C resulted in the formation of orange prisms. A second crop of orange crystals was obtained from the supernatant. Yield: 1.05 g (80%); mp 116–118 °C. Anal. Calcd: C, 53.7, H, 10.2; Cl, 8.4. Found: C, 52.6; H, 10.3; Cl, 8.4. IR (cm^{-1}): 2729 w, 1415 m, 1370 s, 1356 s, 1290 w, 1253 w, 1238 s, 1229 s, 1210 w, 1158 w, 1108 w, 1084 w, 1040 m, 1026 m, 996 w, 959 w, 927 w, 879 m, 857 w, 806 w, 739 w, 720 w, 673 s, 662 s, 615 w, 578 w, 549 w, 471 w, 457 w.

3. Carbonylation of $Fe(CH_2CMe_3)Cl$(dippe). A. 2 equiv of CO: The neopentyl complex $Fe(CH_2CMe_3)Cl$(dippe) (0.11 g, 0.26 mmol) was dissolved in diethyl ether (25 mL). Carbon monoxide (15 mL, approximately 0.6 mmol) was bubbled through the solution by using a syringe. The yellow solution turned red-orange. After being stirred for 1 h, the ether was removed in vacuo and the residue extracted with pentane (40 mL). The solution was filtered, concentrated to ca. 30 mL, and cooled to −20 °C, yielding small red-orange crystals of $Fe(\eta^2\text{-}COCH_2CMe_3)Cl(CO)$(dippe). Yield: 0.05 g (40%). IR (cm^{-1}): 1905 (ν_{CO}), 1596 (ν_{COR}). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): AB spin system, δ_A 105.1 (br s), δ_B 79.4 (br s).

B. 3 atm of CO. The neopentyl complex $Fe(CH_2CMe_3)Cl$(dippe) (0.15 g, 0.35 mmol) was dissolved in diethyl ether (25 mL) in a Fisher-Porter bottle which was then pressurized to 3 atm with carbon monoxide. The yellow solution immediately turned dark orange and then yellow-orange. After being stirred for 2 h, the ether was removed in vacuo and the residue was extracted with pentane (40 mL). The solution was filtered, concentrated to ca. 20 mL, and cooled to −20 °C yielding bright yellow-orange prisms of $Fe(\eta^1\text{-}COCH_2CMe_3)Cl(CO)_2$(dippe). Yield: 0.05 g (30%). IR (cm^{-1}): 2000, 1945 (ν_{CO}), 1625 (ν_{COR}). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): major (95%) isomer, δ 81.8 (s); minor (5%) isomer, AB spin system, δ_A 65.8, δ_B 64.8, J_{AB} = 12.8 Hz.

In a similar manner, the carbonylation was carried out by using 99% enriched ^{13}CO. $^{13}C\{^1H\}$ NMR (only peaks due to the major isomer are reported): δ 18.8, 19.4, 19.7, 19.8 (s, $PCHMe_2$); 21.5 ("t", $^1J_{PC} + {}^2J_{PC}$ = 36.1 Hz, PCH_2); 23.8 ("q", $PCHMe_2$); 29.6 (s, CH_2CMe_3); 30.0 (s, CH_2CMe_3); 32.5 (d, J_{CC} = 1.7 Hz, CH_2CMe_3);

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(51) It is also possible that a unidentate acyl structure analogous to **4** or **5** would be prohibitively crowded due to unacceptably large steric repulsions between the mesityl group and the dippe isopropyl substituents. We thank a reviewer for suggesting this possibility.

(52) Fryzuk, M. D.; Jones, T.; Einstein, F. W. B. *Organometallics* **1984**, *3*, 185-191.

(53) Andersen, R. A.; Wilkinson, G. *Inorg. Synth.* **1979**, *19*, 262-264.

216.1 (18-line pattern, CO); 266.8 (7-line pattern, COCH$_2$CMe$_3$). The ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra were intrepretable as follows: major isomer, AA′XX′Y spin system, δ_A 81.8, δ_X 216.1, δ_Y 266.8, $J_{AA'} = 43.3$, $J_{AX} = 39.2$, $J_{AX'} = -26.0$, $J_{AY} = 15.4$, $J_{XX'} = 10.4$, $J_{XY} = 7.9$ Hz; minor isomer, ABXYZ spin system, δ_A 65.8, δ_B 64.8, δ_X 212.8, δ_Y 215.2, δ_Z 262.2, $J_{AB} = 13.1$, $J_{AX} = 28.5$, $J_{AY} = 49.8$, $J_{AZ} = 16.9$, $J_{BX} = 7.1$, $J_{BY} = 9.4$, $J_{BZ} = 43.1$, $J_{XY} = 11.2$, $J_{XZ} = 8.7$, $J_{YZ} = 8.3$ Hz.

4. Carbonylation of Fe(CH$_2$CMe$_3$)Br(dippe). A. 2 equiv of CO. The neopentyl complex Fe(CH$_2$CMe$_3$)Br(dippe) (0.31 g, 0.66 mmol) was dissolved in diethyl ether (25 mL). Carbon monoxide (30 mL, approximately 1.2 mmol) was bubbled through the solution by using a syringe. The yellow solution turned red-orange and was stirred for 1 h. The ether was removed in vacuo, and the residue was extracted with pentane (40 mL). The solution was filtered, concentrated to ca. 30 mL, and cooled to −20 °C yielding red-orange crystals of Fe(η^2-COCH$_2$CMe$_3$)Br(CO)(dippe). Yield: 0.13 g (38%). IR (cm^{-1}): 1908 (ν_{CO}), 1591 (ν_{COR}). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 25 °C): AB spin system, δ_A 112.2, δ_B 79.6, $J_{AB} = 19.3$ Hz.

In a similar manner the carbonylation was carried out using 99% enriched ^{13}CO. ^{13}C{^{1}H} NMR (C$_7$D$_8$, −40 °C): δ 228.0 ("d", CO); 277.5 (br.s, COCH$_2$CMe$_3$).

B. 3 atm of CO. The neopentyl complex Fe(CH$_2$CMe$_3$)Br(dippe) (0.11 g, 0.23 mmol) was dissolved in diethyl ether (25 mL) in a Fisher-Porter bottle which was then pressurized to 3 atm with carbon monoxide. The yellow solution immediately turned dark orange and then yellow-orange. After being stirred for 2 h, the ether was removed in vacuo and the residue extracted with pentane (40 mL). The solution was filtered, concentrated to ca. 20 mL, and cooled to −20 °C, yielding yellow-orange crystals of Fe(η^1-COCH$_2$CMe$_3$)Br(CO)$_2$(dippe). Yield: 0.07 g (55%). IR (cm^{-1}): 2004, 1959 (ν_{CO}), 1634 (ν_{COR}). ^{31}P{^{1}H}: major (95%) isomer, δ 79.0 (s); minor (5%) isomer, AB spin system, δ_A 62.8, δ_B 60.5, $J_{AB} = 14.5$ Hz.

In a similar manner the carbonylation was carried out by using 99% enriched ^{13}CO. ^{13}C{^{1}H} NMR: δ 18.8, 19.5, 19.6, 19.9 (s, PCHMe_2); 21.7 ("t", $^1J_{PC} + {}^2J_{PC} = 37.7$ Hz, PCH$_2$); 23.6 ("t", $^1J_{PC} + {}^4J_{PC} = 18.1$ Hz, PCHMe$_2$); 25.6 ("t", $^1J_{PC} + {}^4J_{PC} = 21.0$ Hz, PCHMe$_2$); 29.6 (s, CH$_2$CMe_3); 30.2 (s, CH$_2$$CMe_3$); 32.6 (d, $J_{CC} = 2.4$ Hz, CH$_2$CMe$_3$); 216.5 (18-line pattern, CO); 267.4 (7-line pattern, COCH$_2$CMe$_3$).

5. Carbonylation of Fe(C$_6$H$_2$Me$_3$)Br(dippe). The mesityl complex Fe(C$_6$H$_2$Me$_3$)Br(dippe) (0.12 g, 0.23 mmol) was dissolved in toluene (30 mL) in a Fisher-Porter bottle which was then pressurized to 3 atm with carbon monoxide. The yellow solution immediately turned dark orange. After being stirred for 2 h, the solution was filtered, concentrated to ca. 20 mL, and cooled to −20 °C to yield red-orange crystals of Fe(COC$_6$H$_2$Me$_3$)Br(CO)(dippe). Yield: 0.05 g (38%). IR (cm^{-1}): 1910 (ν_{CO}), 1525 (ν_{COR}). ^{1}H NMR (C$_6$D$_6$, 25 °C): δ 0.46 (dd, $J_{PH} = 11.7$, $J_{HH} = 6.9$ Hz, PCHMe_2), 0.65 (dd, $J_{PH} = 13.2$, $J_{HH} = 7.2$ Hz, PCHMe_2), 0.76 (dd, $J_{PH} = 14.3$, $J_{HH} = 7.1$ Hz, PCHMe_2), 0.96 (dd, $J_{PH} = 14.4$, $J_{HH} = 7.2$ Hz, PCHMe_2), 1.15 (dd, $J_{PH} = 13.8$, $J_{HH} = 7.2$ Hz, PCHMe_2), 1.23 (dd, $J_{PH} = 10.8$, $J_{HH} = 7.2$ Hz, PCHMe_2), 1.48 (dd, $J_{PH} = 14.3$, $J_{HH} = 7.1$ Hz, PCHMe_2), 1.65 (dd, $J_{PH} = 16.2$, $J_{HH} = 7.2$ Hz, PCHMe_2), 1.96 (s, p-Me), 2.50 (m, PCHMe$_2$), 2.60 (s, o-Me), 3.04 (m, PCHMe$_2$), 4.14 (s, o-Me), 6.60 (s, m-H), 6.84 (s, m-H). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 25 °C): AB spin system, δ_A 81.8, δ_B 114.7, $J_{AB} = 17.3$ Hz.

In a similar manner, the carbonylation was carried out using 99% enriched ^{13}CO. ^{13}C{^{1}H} NMR (C$_7$D$_8$, −15 °C): ABXY spin system, δ_X 228.0 (CO), δ_Y 260.0 (COR), $J_{XY} = 5.5$, $J_{AX} = 0$, $J_{AY} = 17.7$, $J_{BX} = 27.3$, $J_{BY} = 32.5$ Hz.

Crystallographic Studies. Single crystals of Fe(η^2-COC$_6$H$_2$Me$_3$)Br(CO)(dippe) (**3**), grown from tetrahydrofuran, were sealed in thin-walled glass capillaries under argon. Preliminary photographs yielded rough cell dimensions, and a suitable crystal was transferred to the diffractometer. The crystal chosen was slightly twinned, but this did not interfere with the data collection, although the estimated standard deviations of the unit cell parameters were slightly larger than usual. The overall diffraction pattern was weak, but there was measurable intensity to the upper 2θ limit. Standard peak search and automatic indexing procedures, followed by least-squares refinement using 15 reflections, yielded the cell dimensions given in Table II.

Data were collected in one quadrant of reciprocal space ($\pm h,+k,+l$) using measurement parameters listed in Table II. The space group was unambiguously determined to be $P2_1/n$ from the systematic absences. The measured intensities were reduced to structure factor amplitudes and their estimated standard deviations by correction for background, scan speed, and Lorentz and polarization effects. Crystal decay corrections were applied with no significant change. Absorption corrections were applied, the maximum and minimum transmission factors being 0.639 and 0.471. Only those data with $I \geq 2.58\sigma(I)$ were used in the least-squares refinement. (In view of the successful refinement of the proposed model, no attempt was made to include data at a lower confidence level. The data-to-parameter ratio of 7.0:1 was judged to be low but acceptable.)

The structure was solved by using direct methods and weighted difference Fourier methods. The quantity minimized by the least-squares program was $\sum w(|F_o| - |F_c|)^2$, where $w = 3.90/(\sigma(F_o)^2 + (pF_o)^2)$. The analytical approximations to the scattering factors were corrected for both real and imaginary components of anomalous dispersion. No crystallographic symmetry was imposed on the molecule. In the final cycle of least squares, all non-hydrogen atoms were refined with anisotropic thermal coefficients and a group isotropic thermal parameter was varied for the hydrogen atoms, which were fixed in "idealized" positions with C–H = 0.95 Å; the hydrogen atoms of the mesityl methyl groups were placed in arbitrary rotational conformations about the C–CH$_3$ bonds. Successful convergence was indicated by the maximum shift/error of 0.001 for the last cycle. The thermal coefficients for atoms C2, C6, and C10 converged to chemically unreasonable values; however, attempts to refine a disordered model for atom C2 and the phenyl ring were unsuccessful. The highest residual electron density, 1.05 e/Å^3, in the final differences Fourier map was located 1.67 Å from O2 and 2.16 Å from Br describing an angle of 109° with these two atoms. The remaining peaks above the background in the final map were in the vicinity of the bromine and iron atoms. A final analysis of variance between observed and calculated structure factors showed no apparent systematic errors.

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Registry No. **1**, 111291-09-9; **1**-$^{13}C_3$, 111291-10-2; **2a**, 111291-17-9; **2a**-$^{13}C_2$, 111291-18-0; **2b**, 111291-13-5; **3**, 111291-21-5; **3**-$^{13}C_2$, 111291-22-6; **4a**, 111291-19-1; **4a**-$^{13}C_3$, 111291-20-4; **4b**, 111291-14-6; **4b**-$^{13}C_3$, 111291-15-7; **5a**, 111407-32-0; **5b**, 111407-31-9; **5b**-$^{13}C_3$, 111291-16-8; Fe(CH$_2$CMe$_3$)$_2$(dippe), 106905-32-2; Fe(CH$_2$SiMe$_3$)$_2$(dippe), 106905-31-1; Fe(CH$_2$CMe$_3$)Cl(dippe), 111291-11-3; FeCl$_2$(dippe), 111291-12-4; Fe(CH$_2$CMe$_3$)Br(dippe), 106905-36-6; Fe(C$_6$H$_2$Me$_3$)Br(dippe), 106905-35-5; dineopentyl ketone, 4436-99-1; dineopentylmagnesium, 19978-31-5.

Supplementary Material Available: Tables of hydrogen atom coordinates and complete bond distances and angles for Fe(η^2-COC$_6$H$_2$Me$_3$)Br(CO)(dippe) and observed and simulated ^{31}P{^{1}H} NMR spectra of Fe(η^1-COCH$_2$CMe$_3$)Cl(CO)$_2$(dippe) minor isomer (3 pages); a listing of final observed and calculated structure factors for Fe(η^2-COC$_6$H$_2$Me$_3$)Br(CO)(dippe) (9 pages). Ordering information is given on any current masthead page.