J. Braz. Chem. Soc., Vol. 14, No. 1, 71-75, 2003.
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0103 - 5053 $6.00+0.00

Article

Synthesis and Characterization of $[(CO)_4FeL\text{-}L]$ and $[(CO)_4FeL\text{-}LFe(CO)_4]$ wherein L-L is $N(CH_2CH_2)_3N$ and also $P(NMeNMe)_3P$ in the Latter Complex. Single Crystal X-ray Molecular Structure of $[Fe(CO)_4DABCO]$

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Descrevemos aqui a síntese e caracterização de novos compostos mono- e dinucleares derivados de pentacarbonilferro. Eles foram obtidos através da irradiação UV de $[Fe(CO)_5]$ com o ligante apropriado em THF e foram caracterizados por espectroscopia de RMN de ^1H, ^{13}C, $^{13}C\{^1H\}$, ^{31}P e $^{31}P\{^1H\}$, por especroscopia na região do IV e análise elementar. A estrutura molecular do $[Fe(CO)_4(DABCO)]$ determinada por um estudo de difração de raio-X é descrita. O espectro de RMN de $^{13}C\{^1H\}$ dos complexos revelam fluxionalidade, provavelmente *via* pseudorotação de Berry.

Herein we report the syntheses and characterization of the novel title mono- and dinuclear compounds from pentacarbonyliron. They were obtained in a stepwise manner by UV irradiation of $[Fe(CO)_5]$ with the appropriate ligand in THF and were characterized by ^1H, ^{13}C, $^{13}C\{^1H\}$ ^{31}P and $^{31}P\{^1H\}$ NMR spectroscopy, by IR spectroscopy and by elemental analysis. The single crystal X-ray molecular structure of $[Fe(CO)_4(DABCO)]$ is described. The $^{13}C\{^1H\}$ NMR spectra of each of the title complexes reveal their fluxional behavior, which presumably occurs *via* Berry pseudorotation.

Keywords: DABCO, tetracarbonyliron, NMR spectroscopy

Introduction

With the exception of nitrosyl complexes, mononuclear iron tetracarbonyl complexes bearing nitrogen ligands are relatively rare[1] and most of the reported examples involve aromatic nitrogen ligands such as pyridine,[2-5] picoline,[2] pyrazine,[3] quinoline[2] and lutidine.[2] Several aliphatic trialkylaminetetracarbonyl iron complexes have been reported in which the ligand is NMe_3,[6,7] NEt_3,[6] *n*-NPr_3,[6] *n*-NBu_3,[6] $N(PhCH_2)_2Me$,[6] hexamethylenetetraamine[6] or quinuclidine.[6] The instability of aminetetracarbonyl iron complexes has been attributed to the tendency of nitrogen bases to facilitate disproportionation of iron pentacarbonyl.[4,8-11] In general, amine tetracarbonyliron complexes must be prepared *via* indirect routes, as through the use of $[Fe_2(CO)_9]$,[12] the reaction of $Fe(CO)_5$ with amine oxide[7] and the reaction of $HFe(CO)_4^-$ with NH_2OSO_3 to yield $H_3NFe(CO)_4$.[13]

Herein we report the preparation of $[Fe(CO)_4(DABCO)]$ $[DABCO = N(CH_2CH_2)_3N]$ (**1**), and $\{[Fe(CO)_4]_2(DABCO)\}$ (**2**) directly from $[Fe(CO)_5]$ and $[Fe(CO)_4(DABCO)]$, respectively, under UV photolysis conditions. We also report the preparation of $\{[Fe(CO)_4]_2[P(NMeNMe)_3P]\}$ (**3**).

Experimental Section

General procedures

All reactions were carried out under argon using standard Schlenk techniques, and solvents were freshly distilled under argon before use. 1,4-diaza-byciclo[2.2.2]octane (DABCO) and $[Fe(CO)_5]$ were bought from Aldrich and were used without further purification. 2,3,5,6,7,8-Hexamethyl-2,3,5,6,7,8-hexaaza-1,4-diphospha-bicyclo[2.2.2]octane was prepared according to a previously described method.[14,15] ^1H, ^{13}C and ^{31}P NMR

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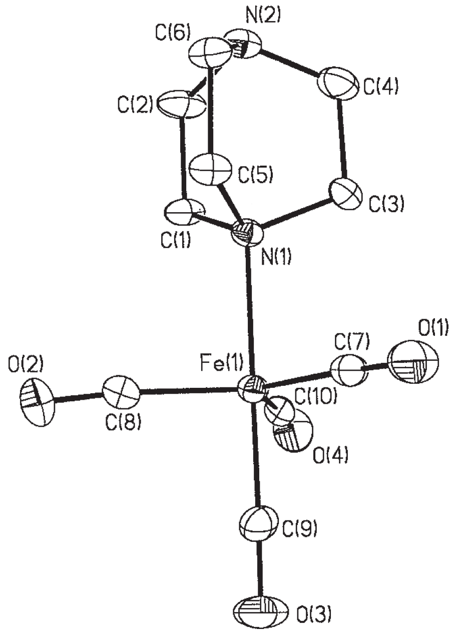

Figure 1. Ortep diagram at 30% probability of **1**. Selected bond distances (Å) and angles (°): Fe(1)-C(9) 1.774(6); Fe(1)-C(7) 1.806(6); Fe(1)-C(8) 1.805(6); Fe(1)-C(10) 1.809(6); Fe(1)-N(1) 2.096(4); C(9)-Fe(1)-C(7) 88.7(2); C(9)-Fe(1)-C(8) 88.3(3); C(7)-Fe(1)-C(8) 119.7(3); C(9)-Fe(1)-C(10) 89.2(3); C(7)-Fe(1)-C(10) 124.1(3); C(8)-Fe(1)-C(10) 116.0(3); C(9)-Fe(1)-N(1) 178.5(2); C(7)-Fe(1)-N(1) 90.02(19); C(8)-Fe(1)-N(1) 91.8(2); C(10)-Fe(1)-N(1) 92.1(2).

spectra were recorded on a Bruker DRX400 spectrometer operating at the indicated frequency and the chemical shifts are quoted in ppm using TMS as an internal standard or H_3PO_4 as an external reference as appropriate. Infrared spectra were recorded on a Bio-Rad FTS-7 FTIR spectrometer and the frequencies are given without correction. Elemental analyses were carried out at Iowa State University. The molecular weight was measured by Schwarzkopf Laboratories using the "osmometric" technique. Melting points (uncorrected) were determined on a Thomas-Hoover capillary melting point apparatus. UV irradiation was carried out using an Ace photochemical reactor containing a Hanovia 7825-34 mercury vapor lamp. The crystal and molecular structure of **1** was carried out by Dr. Ilia Guzei at the University of Wisconsin.

Synthesis of [Fe(CO)$_4$(DABCO)] (**1**)

Three different ratios of ligand to carbonyl (1:1; 2:1 and 1:2) were employed. The last ratio gave the best yield. Thus a Schlenk flask was charged with DABCO (2.00 g, 17.9 mmol), THF (40 mL) and [Fe(CO)$_5$] (7.00 g, 35.7 mmol). The mixture was irradiated for 4 h and then the excess [Fe(CO)$_5$] and the solvent were evaporated under reduced pressure to dryness to yield a red solid that was purified by column chromatography on Florisil and eluted with *n*-hexane. Evaporation of all volatile materials under reduced pressure gave red crystals of the title compound (4.20 g; 84%). mp 98-100 °C, dec., (hexane). ^{1}H NMR data (400.13 MHz, CD$_3$CN 25 °C): δ 2.75 (virt. t, 9.2 Hz separation, 6H), 3.04 (virt t, 9.2 Hz separation, 6H). ^{13}C{^{1}H} NMR (100.62 MHz, CD$_3$CN, 25 °C): δ 48.2 (s, C^A), 59.8 (s, C^B), 217.8 (s, CO). ^{13}C NMR data (100.62 MHz; CD$_3$CN, 25 °C): δ 48.2 (tt, ^1J(CH) 140.9 Hz, ^2J(CH) 5.5 Hz, C^A), 59.8 (tt, ^1J(CH) 141.8 Hz, ^2J(CH) 5.5 Hz, C^B), 217.8 (s, CO). IR ν_{max}/cm^{-1} 2047s, 1960s, 1929w and 1895w (CO) (Nujol). Calc. for $C_{10}H_{12}N_2O_4Fe$: C, 42.89%; H, 4.32%; N, 10.00%. Found: C, 41.09%; H, 4.38%; N, 9.73%. Solution molecular weight determination in CHCl$_3$: 321 (calculated 280).

Synthesis of {[Fe(CO)$_4$]$_2$(DABCO)]} (**2**)

A Schlenk flask was charged with [Fe(CO)$_4$(DABCO)] (**1**) (2.99 g; 10.7 mmol), THF (40 mL) and [Fe(CO)$_5$] (2.10 g; 10.7 mmol). The mixture was irradiated for 48 h and then the solvent was evaporated under reduced pressure to dryness to yield a red solid that was purified chromatographically on Florisil using acetonitrile as eluent. Fractions 1 and 2 from the column were identified as the desired complex and unreacted **1**, respectively. Evaporation of the solvent under reduced pressure from the first fraction gave red crystals of the title compound (3.50 g, 74%). mp120-121 °C, dec.(acetonitrile). ^{1}H NMR (400.13 MHz, CD$_3$CN, 25 °C): δ 3.11 (s). ^{13}C{^{1}H} NMR (100.62 MHz, CD$_3$CN, 25 °C): δ 60.1 (s); 218.2 (s, CO). ^{13}C NMR (100.62 MHz, CD$_3$CN, 25 °C): δ 60.1 (tt, ^1J(CH) 145.68 Hz, ^3J(CH) 5.22 Hz), 218.2 (s, CO). IR ν_{max}/cm^{-1} 2047s, 1967w and 1931s (CO) (Nujol). Calc. for $C_{14}H_{12}N_2O_8Fe_2$: C, 37.50%; H, 2.68%; N, 6.25%. Found: C, 37.95%; H, 2.79%; N, 6.12%.

Synthesis of {[Fe(CO)$_4$]$_2$[P(NMeNMe)$_3$P]} (**3**)

Using a 1:2 ligand-to-metal ratio proved to afford a better yield than a 1:1 ratio and so a Schlenk flask was charged with P(NMeNMe)$_3$P (0.10 g, 0.42 mmol), THF (20 mL) and [Fe(CO)$_5$] (0.17 g, 0.9 mmol). The mixture was irradiated with UV light for 4 h and then unreacted [Fe(CO)$_5$] and the solvent were evaporated under reduced pressure to dryness, affording a pale yellow solid that was purified by chromatography on Florisil using benzene as eluent. Evaporation of the benzene under reduced pressure gave pale yellow crystals of the title compound (0.20 g, 79%). mp 255-257 °C, dec. (benzene). ^{31}P{^{1}H} NMR (162.0 MHz, CDCl$_3$, 25 °C): δ 166.6 (s). ^{31}P NMR (162.0 MHz,

$CDCl_3$, 25 °C): δ 166.6 (m). ^{1}H NMR (400.13 MHz, CD_3CN, 25 °C): δ 3.02 (virt. t, 6 Hz separation, CH_3). $^{13}C\{^1H\}$ NMR (100.62 MHz, $CDCl_3$, 25 °C): δ 37.1 (overlapping dd, $^2J(CP) = {}^3J(CP) = 3.52$ Hz, CH_3), 217.8 (overlapping dd $^2J(CP) = {}^5J(CP) = 10.77$ Hz, CO). ^{13}C NMR (100.62 MHz, $CDCl_3$, 25 °C) δ 37.1 (q of overlapping dd, $^1J(CH)$ 138.14 Hz, $^2J(CP) = {}^3J(CP) = 3.52$ Hz, CH_3), 217.8 (overlapping dd, $^2J(CP) = {}^5J(CP)$ 10.77 Hz, CO). IR ν_{max}/cm^{-1} 2059s, 1992s and 1959vs (CO) (Nujol). Calcd for $C_{14}H_{18}N_6O_8P_2Fe_2$: C, 29.37%; H, 3.15%; N, 14.64%. Found: C, 29.40%; H, 3.23% N, 14.70%.

Structure determination of **1**

Data collection. A yellow crystal was selected under oil under ambient conditions and attached to the tip of a glass capillary. The crystal was mounted in a stream of cold nitrogen at 173(2)K and centered in the X-ray beam by using a video camera. Crystal evaluation and data collection were performed on a Bruker CCD-1000 diffractometer with Mo Kα radiation with a diffractometer to crystal distance of 4.9 cm. The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 20 frames collected at intervals of 0.3° in a 6° range about ω with an exposure time of 10 seconds per frame. A total of 64 reflections were obtained. The reflections were successfully indexed by an automated indexing routine built into the SMART program. The final cell constants were calculated from a set of 6257 strong reflections from the actual data collection. The data were collected using the hemisphere data collection routine. The reciprocal space was surveyed to the extent of a full sphere to a resolution of 0.80 Å. A total of 20682 data were harvested by collecting three sets of frames with 0.3° scans in ω with an exposure time 30 sec per frame. These highly redundant data sets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements.[16]

Structure solution and refinement. The systematic absences in the diffraction data were uniquely consistent for the space group $P2_{1/c}$ which yielded chemically reasonable and computationally stable refinement results.[17] A successful solution by the direct methods provided most non-hydrogen atoms from the E-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. There are two independent molecules of the Fe complex in the asymmetric unit. The final least-squares refinement of 572 parameters 6071 data resulted in residuals *R* (based on F^2 for $I > 2\sigma$) and *wR* (based on F^2 for all data) of 0.0580 and 0.1545, respectively. The final difference Fourier map was featureless. Crystallographic data for **1** are summarized in Table 1.

Table 1. Crystal and structure refinement data for **1**

Empirical formula	$C_{10}H_{12}FeN_2O_4$	
Formula weight	280.07	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	$P2_{1/c}$	
Unit cell	a = 18.2049(9) Å	α = 90°
	b = 10.5585(5) Å	β = 112.020(1)°
	c = 13.8313(7) Å	γ = 90°
Volume	2464.7(2) Å^3	
Z	8	
Density (calculated)	1.510 mg/m^3	
Absorption coefficient	1.227 mm^{-1}	
F(000)	1152	
Crystal size	0.42 x 0.39 x 0.24 mm^3	
Theta range for data collection	2.28 to 26.38°	
Index ranges	-22<=h<=21, 0<=k<=13, 0<=l<=17	
Reflections collected	20682	
Independent reflections	5024 [R(int) = 0.0391]	
Completeness to theta = 26.38°	99.6%	
Absorption correction	empirical with SADABS	
Max. and min. transmission	0.7571 and 0.6267	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	5024/0/307	
Goodness-of-fit on F^2	1.012	
Final R indices [I>2sigma(I)]	R1 = 0.0580, wR2 = 0.1545	
R indices (all data)	R1 = 0.0790, wR2 = 0.1623	
Largest diff. peak and hole	0.787 and -0.462 e. Å^{-3}	

Results and Discussion

The photochemical reaction of [$Fe(CO)_5$] with DABCO in THF affords complex **1** in virtually quantitative yield after 4 h. For periods longer than this, formation of a brown precipitate is observed although interestingly, we observed no evidence for the formation of dinuclear **2** nor for the disubstituted complex [$Fe(CO)_3(DABCO)_2$] in this reaction, even when various ratios of reagents were used. We were able to obtain dinuclear **2** by irradiating **1** for 48 h in the presence of [$Fe(CO)_5$]. However, we were not able to prepare [$Fe(CO)_3(DABCO)_2$] even when a mixture of **1** and excess DABCO was irradiated for 48 h. After this time, a large amount of paramagnetic material was formed. After filtering the THF solution through Florisil, only a mixture containing unreacted materials could be obtained.

Complexes **1** and **2** are remarkably stable in the solid state and they can be manipulated in air for long periods of time. However they decompose very easily in solution, especially in hydrocarbons, producing a brown precipitate. Similar observations have been reported for other aminetetracarbonyl complexes.[4-6]

The ^1H NMR spectrum of **1** in CD_3CN shows two virtual triplets, with band separations of 9.2 Hz corresponding to the two sets of chemically equivalent but magnetically nonequivalent hydrogens on each CH_2CH_2 moiety in DABCO. The virtually coupled triplet at δ 2.75 is assigned to the CH_2 groups bonded to the uncoordinated nitrogen (C^A) due to its proximity to the chemical shift of free DABCO (δ 2.65) whereas the virtually coupled triplet at δ 3.04 is attributed to the CH_2 groups bonded to the coordinated nitrogen (C^B). Complex **1** shows a ^1H NMR spectrum in which the chemical shifts and multiplet patterns are rather solvent dependent. In $CDCl_3$, its ^1H NMR spectrum exhibits two rather broad singlets at δ 2.83 and δ 3.06, and in CD_2Cl_2 broad singlets are also observed (δ 2.78 and δ 3.03). In benzene-d_6 solution, however, the singlets are observed at δ 1.90 and δ 2.33. A somewhat smaller difference in proton chemical shifts is observed for free DABCO in CD_3CN (δ 2.65) compared with benzene-d_6 (δ 2.47).

The $^{13}C\{^1H\}$ NMR spectrum of **1** exhibits two singlets for the two chemically different CH_2 groups in each CH_2CH_2 moiety in DABCO, and their assignments were easily made from its heteronuclear decoupling (HMQC) NMR spectrum or by assuming that the chemical shift closer to that of free DABCO (δ 48.4) would correspond to the CH_2 bonded to the uncoordinated nitrogen, *i.e.* δ 48.2 (C^A) rather than δ 59.8 (C^B). The carbonyl region revealed only one signal for the two types of CO groups, suggesting fluxionality which is rapid on the NMR time scale, a phenomenon commonly observed for substituted pentacarbonyl complexes,[3,18-20] and also for $[Fe(CO)_5]$ which is stereochemically nonrigid on the NMR time scale even at –170 °C.[15,21] Our conclusion on this point for **1** is supported by its $^{13}C\{^1H\}$ NMR spectrum which maintains a singlet for the CO groups down to –80 °C. The process is generally assumed to proceed through Berry pseudorotation which, because bond rupture is not involved, spin-spin coupling is preserved.[3,12,15,17] It had been believed at one time that exchanging one CO with a ligand different in its σ-donor and π-acceptor properties (*e.g.*, pyridine) would inhibit pseudorotation by virtue of a strong σ-donor capability and its extremely weak π-acceptor property, which would create a preference for the ligand to bond in an axial position. However, the ^{13}C NMR spectrum of $[Fe(CO)_4py]$ showed no change from room temperature to temperatures as low as –100 °C.[3] The ^{13}C NMR spectrum of **1**, as expected, shows two triplets of triplets for each CH_2 group (with $^1J_{CH}$ and $^3J_{CH}$ coupling constants in the expected range) and a singlet for the CO groups.

The IR spectrum of **1** exhibits four bands in the CO region (see Experimental) with the lowest reciprocal wave length displaying a very weak intensity. For a complex of C_{3v} symmetry only three bands are normally expected unless splitting of the E mode occurs.[22] The normally axial ligand placement in $Fe(CO)_4L$ complexes has been amply documented by X-ray diffraction studies,[23-25] including $[Fe(CO)_4(PHPh_2)]$, for example, for which splitting of the E mode has also been observed.[21]

Despite the tendency for tetracarbonyl iron(0) amine complexes to decompose in hydrocarbon solvents,[4-6] a yellow single crystal of **1** suitable for X-ray study was obtained from an *n*-hexane solution of this complex. The molecular structure of **1** (Figure 1) is a trigonal bipyramid with the DABCO ligand in an axial position, as would be expected due to the lack of π-acceptor character of the ligand. The Fe-N bond length [2.096(4) Å] is longer than in $[Fe(CO)_4(pyridazine)]$ [2.013(5) Å],[26] $[Fe(CO)_4(py)]$ [2.046(5) Å],[3] $[Fe(CO)_4(pyrazine)]$ [2.031(2) Å][3] and $[CpFeC_5H_4\text{-}4\text{-}CHCH\text{-}py\text{-}Fe(CO)_4]$[2.041(4) Å][27] by more than three times the esd values. However, this is not unexpected since in complex **1** the donating nitrogen lone pair has sp^3 character whereas the examples cited possess nitrogens with an sp^2 lone pair in which the s character is augmented. To the best of our knowledge, **1** represents the first example of a complex of the type $[Fe(CO)_4(amine)]$ whose structure has been determined by X-ray crystallographic means in which the amine is aliphatic. The $Fe\text{-}C_{(ax)}$ bond distance [1.774(6) Å] found for complex **1** is very close to those in $[Fe(CO)_4(pyridazine)]$ [1.765(7) Å],[26] $[Fe(CO)_4(py)]$ [1.772(7) Å],[3] $[Fe(CO)_4(pyrazine)]$ [1.774(4) Å][3] and $[CpFeC_5H_4CHCH\text{-}py\text{-}Fe(CO)_4]$ [1.760(6) Å].[27] The $Fe\text{-}C_{(eq)}$ bond distances (avg. 1.807 Å) are in the normal range found for complexes of the type $[Fe(CO)_4L]$.[3,26,27]

The dinuclear complex **2** features a singlet at δ 3.11 in its ^1H NMR spectrum, corresponding to the two chemically equivalent CH_2 groups. Its $^{13}C\{^1H\}$ NMR spectrum consists of a singlet due to the CH_2 groups (δ 60.1) and, similarly to the $^{13}C\{^1H\}$ NMR spectrum of **1**, only one signal corresponding to the CO groups at (δ 218.2) is present. The ^{13}C NMR spectrum of this compound displays a triplet of triplets at δ 60.1 with a one-bond HC coupling constant of 145.68 Hz and a three-bond proton-carbon coupling constant of 5.22 Hz. As expected, the CO ^{13}C resonance appears as a singlet at δ 218.2 owing to rapid pseudorotation. The IR spectrum of **2** reveals three bands in the CO region (2047, 1967 and 1931 cm^{-1}).

Unlike DABCO, $P(NMeNMe)_3P$ in the presence of $[Fe(CO)_5]$ under photolysis conditions does not yield the corresponding mononuclear complex $\{[Fe(CO)_5][P(NMeNMe)_3P]\}$ even when the reaction is carried out with a 1:1 ratio of the reactants. The products isolated from the reactions using a 1:1 or 1:2 ligand-to-metal ratio are the same, namely, $\{[Fe(CO)_5]_2[P(NMeNMe)_3P]\}$ (**3**) in the latter case and excess ligand in the former. The $^{31}P\{^1H\}$ NMR spectrum of **3** shows a singlet at δ 166.6 whereas the ^{31}P NMR spectrum consists of a multiplet containing nine bands centered at the same chemical shift, corresponding to the X part of an $A_9XX'A_9'$ virtually coupled second order spectrum. The ^1H NMR spectrum of **3** exhibits a virtually coupled triplet (indicative of strong PP coupling) corresponding to the A part of an $A_9XX'A_9'$ spectrum at δ 3.02 with a band separation of 6 Hz. Its $^{13}C\{^1H\}$ NMR spectrum consists of two apparent triplets (δ 37.1 and δ 217.8). We assign the upfield triplet to the CH_3 protons which are coupled equally to the two phosphorus atoms ($^2J_{CP} = {}^3J_{CP} = 3.52$ Hz) giving rise to an overlapping pair of doublets. Similarly, the low-field triplet is attributed to accidentally equal coupling of the CO carbons to the two phosphorus nuclei ($^2J_{CP} = {}^5J_{CP} = 10.77$ Hz). While it may seem odd that the five-bond CP coupling is approximately as large as its two-bond counterpart, it should be noted that there are three through-bond pathways for the latter coupling to occur. That spin-spin coupling in a diphosphorus cages of this type can indeed be substantial and is supported by the observation that the PP coupling in $P(CH_2NMe)_3P$ is 27 Hz and is 116 Hz in $S{=}P(CH_2NMe)_3P{=}S$.[28] Like the DABCO complexes **1** and **2**, complex **3** is also fluxional on the NMR time scale, since only one ^{13}C chemical shift (δ 217.8) is observed.

Acknowledgements

We thank the Donors of the PRF administered by the American Chemical Society for funding this work. RMM thanks CNPq-Brazil for a travel award and UFMG for the award of a sabbatical year.

Supplementary Material

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no CCDC 176925. Copies of the data can be obtained, free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or e-mail: deposit@ccdc.cam.ac.uk).

References

1. Whitmire, K. H. In *Comprehensive Organometallic Chemistry II*; Abel; E. A.; Stone, F. G. A.; Wilkinson, G., eds.; Elsevier Science: Oxford, UK, 1995, vol. 7, p.1.
2. Shubert, E. H.; Sheline, R. K.; *Inorg. Chem.* **1966**, *5*, 1071.
3. Cotton, F. A.; Troup, J. M.; *J. Am. Chem. Soc.* **1974**, *96*, 3438.
4. Fanchinetti, G.; Fochi, G.; Funaioli, T.; Zanazzi, P. F.; *J. Chem. Soc., Chem. Commun.* **1987**, 87.
5. Mealli, C.; Proserpio, D. M.; Fachinetti, G.; Funaioli, T.; Fochi, G.; Zanazzi, P. F.; *Inorg. Chem.* **1989**, *28*, 1122.
6. Birencwaig, F.; Shamai, H.; Shvo, Y.; *Tetrahedron Letters* **1979**, *31*, 2947.
7. Elzinga, J.; Hogeveen, H.; *J. Chem. Soc., Chem. Commun.* **1977**, 705.
8. Hieber, W.; Werner, R.; *Chem. Ber.* **1957**, *90*, 286.
9. Hieber, W.; *Angew. Chem.* **1960**, *72*, 795.
10. Hieber, W.; Kahlen, R.; *Chem. Ber.* **1958**, *91*, 2223.
11. Edgell, W. F.; Yang, M. T.; *J. Am. Chem. Soc.* **1966**, *88*, 4839.
12. Shriver, D. F.; Whitmire, K. H., In *Comprehensive Organometallic Chemistry*, Wilkinson, G.; Stone, F. G. A.; Abel, E. W. eds., Pergamon Press: Oxford, UK, 1982, vol. 4, p. 243.
13. Hieber, W.; Beutner, H.; *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 116.
14. Goetze, R.; Nöth, H.; Payne, D. S.; *Chem. Ber.* **1972**, *105*, 2637.
15. Nöth, H. ; Ullmann, R.; *Chem. Ber.* **1974**, *107*, 1019.
16. Blessing, R. H.; *Acta Cryst.* **1995**, *A51*, 33.
17. All software and sources of the scattering factors are contained in the *SHELXTL (version 5.1)* program library (G. Sheldrick, Bruker Analytical X-Ray Systems, Madison, WI).
18. Adams, R. D.; Cotton, F. A.; In *Dynamic Nuclear Magnetic Resonance Spectroscopy*, Jackman, L. M.; Cotton,F. A., eds., Academic Press: New York, 1975, p. 489.
19. Udovich, C. A.; Clark, R. J.; Hass, H.; *Inorg. Chem.* **1969**, *8*, 1066.
20. Langford, G. R.; Akhtar, M.; Ellis, P. D.; MacDiarmid; A. G.; Odom, J. D.; *Inorg. Chem.* **1975**, *98*, 5728.
21. Jesson, J. P.; Meakin, P.; *J. Am. Chem. Soc.* **1973**, *95*, 1344.
22. Darensbourg, D. J.; Nelson, III, H. H.; Hyde, C. L.; *Inorg. Chem.* **1974**, *13*, 2135.
23. Riley, P.; Davis, R. E; *Inorg. Chem.*, **1980**, 19, 159.
24. Pickardt, J.; Rosch, L.; Schumann, H.; *J. Organomet. Chem.* **1976**, *107*, 241.
25. Kilbourn, B. T.; Raeburn, U. A.; Thompson, D. T.; *J. Chem. Soc. (A)* **1969**, 1906.
26. Cotton, F. A.; Hanson, B. E.; *Isr. J. Chem.* **1977**, *15*, 165.
27. Lee, I. S.; Lee, S. S.; Chung, Y. K.; Kim, D.; Song, N. W.; *Inorg. Chim. Acta*, **1998**, *279*, 243.
28. P. M. Stricklen; J.G. Verkade, unpublished work.

Received: June 21, 2002
Published on the web: December 13, 2002