π-orbital interaction is donor or acceptor, but are quite sensitive to strong σ-donor interactions, to the point where large g_{max} EPR spectra can be observed even in the presence of a single planar ligand.

In summary, the electronic structures of bis(nitro) and mixed-axial-ligand mono(nitro) iron(III) porphyrinates have been examined by Mössbauer and EPR spectroscopies. The electronic structure is dominated by the strong π-acceptor character of N-bound nitrite, which can be deduced by the relatively large rhombicities (difference in energy of the d_{xz} and d_{yz} orbitals).

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Supplementary Material Available: Tables SI–SVIII, giving complete crystallographic details, anisotropic thermal parameters, fixed hydrogen atom positions, and complete bond distances and angles for [Fe(NO_2)(Py)(TpivPP)] and [Fe(NO_2)(HIm)(TpivPP)], Figure S1, showing a mean plane diagram for [Fe(NO_2)(HIm)(TpivPP)], and Figures S2 and S3, showing nitrite, imidazole, and pyridine orientations (16 pages); listings of observed and calculated structure amplitudes (×10) for both compounds (37 pages). Ordering information is given on any current masthead page.

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Use of Solid-State ^{13}C NMR Spectroscopy to Quantify the Degree of Asymmetry of Bonding for Semibridging CO Groups in Iron Carbonyl Complexes

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The solid-state ^{13}C NMR spectra of some substituted iron carbonyl complexes have been analyzed to give values for the carbonyl carbon chemical shift tensor components. It is shown that the lowest frequency tensor component and the chemical shift anisotropy correlate with the degree of bonding asymmetry in double-bridging carbonyl groups, whereas the ^{13}C isotropic chemical shift does not correlate. The correlations are proposed to form the basis for a method of estimating iron–carbon bond lengths for μ_2-CO groups in this type of complex.

Introduction

Infrared (IR) spectroscopy is widely used in the study of metallocarbonyl complexes; in particular the C–O bond stretching frequency may be directly correlated with the metal–carbon bonding. As described by Cotton and Wilkinson,[2] terminal carbonyl groups (M–CO) in neutral molecules generally absorb in the region 1850–2125 cm^{-1}, while bridging CO groups absorb in the region 1700–1860 cm^{-1}. Isotropic ^{13}C shieldings measured from either solution or solid-state NMR spectra may also be diagnostic of the bonding. These observations are typified by data for $Fe_2(CO)_4(\eta^5\text{-}C_5H_5)_2$ (I), which in octane solution has IR absorptions at 1794 cm^{-1} due to symmetric double bridging CO groups and at 1961 and 2005 cm^{-1} due to terminal CO groups[3] and has solution ^{13}C chemical shifts at 273.2 (bridging CO) and 210.2 ppm (terminal CO).[4] For *semibridging* CO groups which are shared unequally between two iron atoms (Fe_b- - -CO–Fe_a) the frequencies of the IR absorptions may not be so readily interpreted in terms of degree of bridging character or asymmetry. It is known that the isotropic ^{13}C chemical shifts for asymmetric briding CO groups may occur between the extremes exhibited by the bridging and terminal groups of I; for example the asymmetric bridging CO group in $Fe_3(CO)_8(PhC_2Ph)_2$ has its ^{13}C chemical shift at 253.7 ppm.[5] However the symmetric bridging CO group of $Fe_2(CO)_9$ has its ^{13}C resonance at 235.9 ppm.[6] Clearly, the exact value for the isotropic ^{13}C shift does not reflect the *degree* of symmetry in the bridging. The present study is concerned with the analysis of the slow magic angle spinning (MAS) solid-state ^{13}C spectra to provide the principal components of the chemical shift tensor (δ_{11}, δ_{22}, δ_{33}) and the chemical shift anisotropy ($\Delta\delta$, see below) as well as the ^{13}C isotropic shift (δ_{iso}), and the investigation of possible correlations between these additional parameters and the degree of bridging asymmetry. Recently, Carty et al.[7] reported correlations between the ^{31}P chemical shift tensor components and M–P–M (M = Fe, Ru, Os) bond angles in a series of phosphido-bridged complexes.

Experimental Section

Materials. All carbonyl complexes employed in this study were ^{13}CO enriched. *cis* and *trans*-$Fe_2(CO)_4(\eta^5\text{-}C_5H_5)_2$ (I) were obtained as a commercial mixture (Strem Chemicals), and ^{13}C enrichment was performed on the commercial product by heating at 60 °C (*n*-hexane as solvent) under ca. 1 atm 99% ^{13}CO gas for 2 days in sealed vials. The enrichment achieved was ca. 35–40%. The cis isomer was obtained by crystallization from a dichloromethane solution, and the trans isomer from an *n*-heptane solution. $Fe_2(CO)_6PhC_2Ph$ (II), the black isomer of $Fe_3(CO)_8(PhC_2Ph)_2$ (III), and $Fe_3(CO)_{11}PPh_3$ (IV) were all prepared from ^{13}C-enriched $Fe_3(CO)_{12}$ by the methods of Hubel and Braye,[8] Dodge and Schomaker,[9] and Angelici and Siefert,[10] respectively. The phosphine complex (IV) was purified by crystallization from chloroform/pentane at −20 °C. ^{13}C-enriched $Fe_2(CO)_9$ (V) was prepared by irradiation of a solution of ^{13}C-enriched iron pentacarbonyl in acetic acid using a 125-W high-pressure mercury lamp for 24 h. The enrichment of the iron pentacarbonyl (ca. 40% ^{13}C) was achieved by using the procedure of Shore and co-workers[11] with $NaBH_4$ as exchange promoter. The preparation of ^{13}C-enriched $Fe_3(CO)_{12}$ (VI) has been described previously.[12] Levels of ^{13}C enrichment were estimated by using mass spectrometry.

NMR Spectra. Solid-state ^{13}C spectra were recorded by using the cross polarization/magic angle spinning (CP/MAS) technique at 50.3 MHz (Bruker CXP-200) and 75.5 MHz (Bruker MSL-300) as previously described.[12,13] Samples (typically 100–200 mg) were contained

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Table I. ^{13}C Chemical Shift Data[a] and Metal–Carbon Distances for I–VI

compd	δ_{iso}	δ_{11}	δ_{22}	δ_{33}	$\Delta\delta$	η	r_1, r_2[b]
cis-I[c]	272.3	332	305	179	139	0.29	1.91, 1.92
	213.4	361	361	−82	443	0	1.73
	211.5	359	359	−84	443	0	1.76
trans-I[d]	275.7	344	299	184	137	0.50	1.91, 1.92
	212.2	388	334	−86	448	0.18	1.75
II[e]	223.4	365	322	−17	360	0.18	1.73, 2.47
	214.1	351	351	−61	412	0	1.76 ± 0.02 (av of 5 values)
	211.6	349	349	−64	413	0	
	211.0						
	207.0	346	346	−70	416	0	
III[f]	254.9	338	315	111	216	0.16	1.84, 1.99
	253.8	362	302	97	235	0.38	1.77, 1.99
	207.2	350	350	−78	428	0	1.73 ± 0.04 (av of 6 values)
	204.6	344	344	−75	419	0	
	203.9	349	349	−86	435	0	
	202.9	341	341	−74	415	0	
IV[g]	244.5	337	291	104	211	0.32	1.87 ± 0.03
	243.3						2.04 ± 0.03
V[h]	236.9	305	249	157	120	0.70	2.02, 2.02
	205.5	354	339	−77	423	0.12	
VI[i]	238.8						1.96, 2.11
	236.5						1.93, 2.21

[a] Chemical shifts are in ppm, and metal carbon distances in Å; spectra of *cis*- and *trans*-I, II, IV, and V were measured at 75.46 MHz (Bruker MSL-300), and the spectrum of III, at 50.3 MHz (Bruker CXP-200). Estimates of the errors on the chemical shift parameters are given in the Results section. [b] For bridging carbonyls, the two carbon–metal distances are given and for terminal carbonyls, the bond distance is given, the closest approach of a second iron atom being >3.5 Å in all cases. [c] NMR data this work; distances from ref 19. [d] NMR data this work; distances from ref 20. [e] NMR data from this work and ref 13; distances from ref 21. The shielding tensor components for the resonance at 223.4 ppm are slightly different from ref 13, as the spectrum was remeasured. [f] NMR data from ref 12; distances from ref 9. [g] NMR data this work; distances from ref 22. [h] NMR data this work; distances from ref 23. [i] NMR data from ref 18; distances from ref 25.

in 7 mm o.d. rotors of zirconia, and spinning rates, in the region 2500–4000 Hz, were adjusted to minimize overlap between center-band and sideband ^{13}C resonances. The 75.5-MHz ^{13}C spectra of V was acquired using the one-pulse method with MAS, with a relaxation delay of 100 s between successive scans. Chemical shifts (δ scale, high frequency positive) were referenced to external neat liquid tetramethylsilane (TMS). Our Herzfeld–Berger analysis[14] of the spinning sideband patterns to obtain chemical shift tensor components is computer-automated in a manner described elsewhere.[12]

Results

The complexes studied here are *cis*- and *trans*-$Fe_2(CO)_4(\eta^5\text{-}C_5H_5)_2$ (I); the iron carbonyl (alkyne) complex $Fe_2(CO)_6PhC_2Ph$ (II) and the black isomer of $Fe_3(CO)_8(PhC_2Ph)_2$ (III); $Fe_3(CO)_{11}PPh_3$ (IV); $Fe_2(CO)_9$ (V); and $Fe_3(CO)_{12}$ (VI). The solid-state slow MAS ^{13}C spectral data for the complexes I–VI are collected in Table I. Isotropic ^{13}C chemical shifts were measured directly from the center-band resonances in the spectra, and the intensities of the spinning sidebands from each resolved center-band resonance were analyzed by the method of Herzfeld and Berger,[14] as we have previously described.[12] This analysis yields the principal elements of the *nuclear shielding* tensor (σ_{11}, σ_{22}, σ_{33}) for each resolved resonance, with the convention $\sigma_{33} \geqslant \sigma_{22} \geqslant \sigma_{11}$. The isotropic shielding (σ_{iso}) is given by

$$\sigma_{iso} = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3 \qquad (1)$$

For the compounds studied here these shielding components happen to agree with the Haeberlen convention:[15] $|\sigma_{33} - \sigma_{iso}| \geqslant |\sigma_{11} - \sigma_{iso}| \geqslant |\sigma_{22} - \sigma_{iso}|$. We here use the normal chemical convention and quote chemical shifts ($\delta_{ii} = -\sigma_{ii}$, $\delta_{iso} = -\sigma_{iso}$). The chemical shift anisotropy, $\Delta\delta$, and asymmetry, η, are given by

$$\Delta\delta = \delta_{33} - (\delta_{11} + \delta_{22})/2 \qquad (2)$$

$$\eta = (\delta_{22} - \delta_{11})/(\delta_{33} - \delta_{iso}) \qquad (3)$$

Dorn et al.[6] have previously reported the solid-state isotropic ^{13}C shifts for *cis*- and *trans*-I, without analyzing the spectra for shift tensor components. In addition Gleeson and Vaughan[16] reported the static solid-state ^{13}C spectrum of I and determined the chemical shift tensor components for the terminal and bridging CO groups, but without resolution of the cis and trans isomers. Therefore we measured the slow MAS spectra of the individual isomers, with the results shown in Table I. The isotropic shifts are identical with those reported by Dorn et al.,[6] and the shift tensor components are close to the values of Gleeson and Vaughan.[16] The values in Table I for δ_{11} and δ_{22} of the terminal carbons of *cis*- and *trans*-I differ somewhat from the values previously reported.[17] However we have considered in detail[12] the errors associated with the estimation of δ_{ii} values using the Herzfeld and Berger[14] method and concluded that these errors are greatest for situations of near-axial symmetry in the chemical shift tensor ($\delta_{11} \cong \delta_{22}$). For example, if we use the experimental data for the terminal CO resonance (δ_{iso} = 212.2 ppm) of *trans*-I in our Herzfeld–Berger analysis and constrain a solution that is axially symmetric ($\delta_{11} = \delta_{22}$), then the quality of the fit is not significantly degraded and we obtain the values $\delta_{11} = \delta_{22} = 359$, $\delta_{33} = -81$, $\Delta\delta = 440$ ppm, and $\eta = 0$. The change in δ_{11} and δ_{22} can, therefore, be quite large (20–30 ppm), while δ_{33} and $\Delta\delta$ are not greatly affected. In addition it is worth noting that the asymmetry parameter changes significantly, and for this reason, in the case of axial or near-axial symmetry, the errors on δ_{11}, δ_{22}, and η are too large to make them diagnostically useful parameters to describe the bonding. We consider that reasonable estimates of the errors on the chemical shift parameters in Table I may be generalized from our previous[12] error analysis on the shielding tensor components of III using error method B (10%) of that study. Those error estimates may be summarized as follows: for axially symmetric chemical shift tensors δ_{11}, δ_{22} ± 11.5, δ_{33} ± 5.3, $\Delta\delta$ ± 9.8 ppm, and $\eta = 0 \pm 0.06$; and for nonaxially symmetric tensors δ_{11} ± 6.5, δ_{22} ± 8.0, δ_{33} ± 5.5, $\Delta\delta$ ± 7.5 ppm, and, for the two examples investigated for III, $\eta = 0.38 \pm 0.01$ and 0.06 ± 0.13.[12]

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The NMR data for II given in this work are slightly different from those previously reported by us,[13] as the spectrum for this study was remeasured by using a higher field spectrometer. NMR data for III are from our[12] earlier work, data for IV and V are new, and the isotropic shifts for VI are from Hanson et al.[18]

Discussion

Structures and IR Spectra of the Complexes. The X-ray structure of *cis*-I shows one molecule in the asymmetric unit, and the two bridging carbonyl groups in the molecule are effectively symmetric with the average Fe–C distance 1.917 Å and Fe–C–Fe angle 82.6°,[19] and the structure of *trans*-I shows half a molecule in the asymmetric unit with the symmetric bridging CO groups having Fe–C distance 1.910 Å and Fe–C–Fe angle 82.9°.[20]

The X-ray structure of II shows the asymmetric unit to be one molecule with five terminal CO groups and a CO group with weak bridging character having Fe–C distances 1.73 and 2.47 Å and Fe–C–Fe angle 71.3°.[21] However, this asymmetry is not obvious from the IR spectrum, which shows absorptions in the range 1923–2062 cm^{-1}.[8] The X-ray structure of III shows one molecule per asymmetric unit with six terminal CO groups and two strongly bridging CO groups with C–Fe distances 1.84, 1.99 Å and 1.77, 1.99 Å and Fe–C–Fe angles 71.5 and 80.5°, respectively;[9] the IR absorptions (1852, 1976, 2021, 2066 cm^{-1}) are indicative of both bridging and terminal CO groups.[8] The X-ray structure of IV shows two molecules per asymmetric unit which are structural isomers of one another.[22] Each isomer has two semibridging and nine terminal carbonyls: the semibridging groups have four short Fe–C distances of 1.87 ± 0.03 Å, four long Fe–C distances of 2.04 ± 0.04 Å, and Fe–C–Fe angles in the region 81–83°. The IR spectrum shows four terminal CO absorptions in the region 1949–2086 cm^{-1} and three bridging absorptions in the region 1795–1836 cm^{-1}.[9] Therefore the IR spectra for III and IV do indicate the presence of bridging carbonyls but the relative numbers of bridging and terminal carbonyls are not easily found.

The X-ray structure of V shows symmetric bridging CO groups with the Fe–C distances 2.016 Å and Fe–C–Fe angles 77.6°,[23] and the IR spectrum shows absorption due to bridging CO at 1821 cm^{-1}.[24] $Fe_3(CO)_{12}$ (VI) has two asymmetric bridging carbonyls with Fe–C distances 1.93, 2.21 Å and 1.96, 2.11 Å and with Fe–C–Fe angles 76.0 and 77.8°, respectively.[25] The IR absorption at ca. 1850 cm^{-1} for VI in both solution and solid state is assigned to bridging CO.[26] It is clear from the above data that IR spectroscopy can give some information on the nature of the CO groups but does not allow a definitive description of the bonding.

Solution-State ^{13}C NMR Spectra. The solution-state ^{13}C NMR spectra at low temperature of the CO groups of *cis*- and *trans*-I show separate resonances due to terminal and symmetrical bridging groups,[4] and the CO groups of II at ambient temperature have ^{13}C resonances at 206.6, 207.8, and 210.5 ppm due to terminal groups and one at 216.5 ppm averaged by rapid exchange between terminal and semibridging positions.[27] For III the solution ^{13}C spectrum shows two resolved resonances due to the six terminal CO groups at 203.1 and 204.8 ppm and one resonance due to the two semibridging carbonyls at 253.8 ppm.[5] $Fe_2(CO)_9$ (V) is insufficiently soluble to yield a solution-state ^{13}C spectrum, while in solution VI displays just one averaged ^{13}C resonance down to −120 °C due to rapid bridge-terminal exchange.[28] The solution-state NMR data offer an improvement over IR data because it is easier to quantify the NMR spectra. However there are still problems arising from a lack of solubility or from rapid intramolecular rearrangements in solution that can prevent the classification of the CO group bonding.

Solid-State ^{13}C NMR Spectra. An advantage of the solid state is that fluxional processes are often much slower in the solid state than in solution, leading to resolution of chemical shifts which may be averaged in solution. In addition the solid-state spectra provide three shift parameters for every ^{13}C resonance. Before proceeding with a detailed discussion of the chemical shift tensor components, we will briefly comment on the main features of the spectra of each of the complexes.

The asymmetric unit in the crystal of *cis*-I is one molecule,[19] and accordingly, the solid-state ^{13}C spectrum shows two terminal CO isotropic shifts (211.8 and 213.4 ppm) with the expected two doubly bridging CO resonances coincident at 272.3 ppm. The asymmetric unit of *trans*-I is half a molecule, and the ^{13}C spectrum shows single terminal and bridging CO resonances at 212.3 and 275.7 ppm, respectively, and for both cis and trans isomers the solid state isotropic chemical shifts are very similar to the solution state (see Introduction). In the solid state, the asymmetric unit for $Fe_2(CO)_6PhC_2Ph$ (II) is one molecule,[21] and in the solid-state ^{13}C spectrum, the center-band resonance for the weakly bridging carbonyl is found at 223.4 ppm with resolution of four of the expected five terminal resonances in the range 207.0–214.1 ppm. Clearly, in the solid state there is a slowing of the intramolecular rearrangement which in solution averages the chemical shift of the bridging carbonyl with a terminal position. The asymmetric unit for $Fe_3(CO)_8(PhC_2Ph)_2$ (III) is also one molecule[9] and the solid-state ^{13}C spectrum shows two resonances for the semibridging groups at 253.8 and 254.9 ppm with resolution of four of the expected six terminal resonances in the region 202.9–207.2 ppm, and the chemical shift regions for these resonances correspond closely to the solution-state values.[12] The solid-state ^{13}C spectrum of $Fe_3(CO)_{11}PPh_3$ (IV) shows two closely spaced resonances at 243.3 and 244.5 ppm, which we assign to the semibridging carbonyls in the asymmetric unit, with eight other resolved resonances in the region 201.7–219.0 ppm. Our solid-state ^{13}C spectrum therefore is consistent with the presence of a single isomer of IV with one molecule in the asymmetric unit. This is in contrast to the X-ray structural analysis of Dahm and Jacobson[22] who found the asymmetric unit to be a pair of structural isomers which differ in the position of the PPh_3 groups. We speculate that the difference between our sample of IV and that used by Dahm and Jacobsen[22] may arise from a different final step in the preparation—we employed crystallization from chloroform/pentane at −20 °C, while the earlier workers used evaporation of a pentane solution.[22] However since the structures of those two isomers were very similar, particularly with respect to the bridging carbonyls, it does not matter for the purpose of this discussion which isomer our sample happens to be. The isotropic ^{13}C resonances of $Fe_2(CO)_9$ were reported at 204.5 and 235.9 ppm for terminal and symmetrical bridge CO groups, respectively, but no analysis was made for the chemical shift tensor components.[6] Our slow MAS spectrum of V showed center-band ^{13}C resonances at 205.5 and 236.9 ppm. The room-temperature solid-state ^{13}C spectrum of $Fe_3(CO)_{12}$ (VI) shows six resolved resonances, reflecting a marked slowing of the rapid intramolecular rearrangement[12,18] that, in solution, averages the ^{13}C resonances to a single chemical shift (vide supra). However, the solid-state ^{13}C spectrum is temperature dependent and at low temperature Hanson et al.[18] reported resonances at 236.5 and 238.8 ppm assignable to the two distinct asymmetric bridging carbonyls in the molecule but did not determine the chemical shift tensor components.

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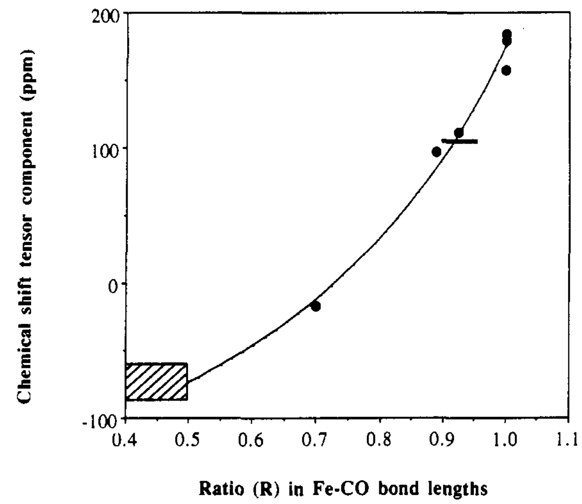

Figure 1. Plot of the lowest frequency chemical shift tensor components (δ_{33}) for the CO groups vs the ratio (R) in Fe–CO bond lengths. Rms deviation between calculated curve (—) and experimental chemical shift = 8.7 ppm.

NMR Correlations with CO Bridge Asymmetry. In view of the success of Carty et al.[7] in correlating solid-state ^{31}P NMR data from phosphido-bridged metal complexes with the metal–P–metal bond angle we investigated first correlations involving the Fe–C–Fe angles (α) in the complexes I–VI, i.e. correlations between the Fe–C–Fe angles and isotropic ^{13}C chemical shift (δ_{iso}), chemical shift anisotropy ($\Delta\delta$), and the lowest frequency chemical shift tensor component (δ_{33}), respectively. For all three trial correlations (particularly for δ_{iso} and δ_{33}) the data for IV appeared out of line with the general trend, and in addition, the values of $\Delta\delta$ and δ_{33} for $Fe_2(CO)_9$ (V) did not conform. Our attempts to compare δ_{11} or δ_{22} with the angle α did not give any reasonable correlations. In seeking an alternative correlation for the carbonyl bridging we noted three points. First, the obvious one that the previous success employing the metal–P–metal bond angle was for a very different bridging ligand to the carbonyls we are investigating.[7] Second, the X-ray structures of the phosphido complexes showed[29] that all the examples used by Carty et al.[7] were symmetrical or very nearly symmetrical phosphido bridges, whereas the bridging carbonyl ligands in this study vary from the symmetric I and V to the highly asymmetric II. The third point is that, with an asymmetric bridge carbonyl, the Fe–C–Fe atoms describe a triangle which requires *three* independent parameters for definition of its geometry, and the Fe–C–Fe bond angle is just one of these three. An alternative basis for a correlation is between the solid-state NMR data (δ_{iso}, δ_{11}, δ_{22}, δ_{33}, $\Delta\delta$, η) in turn with the three interatomic distances (Fe_a–C, Fe_b–C, Fe_a–Fe_b) that define the bridging triangle for each complex, and again we did not find any reasonable correlations. However the situation is different when the structural parameter in the trial correlation is a direct measure of the CO group bridging asymmetry, i.e. the difference (D) between the two Fe–C distances or the ratio (R) of the shorter to the longer of the Fe–C distances. If r_1 and r_2 are the two Fe–C distances, then

$$D = r_2 - r_1 \tag{4}$$

$$R = r_1/r_2 \tag{5}$$

which rearrange to

$$r_2 = r_1/R \tag{6}$$

$$r_1 = DR/(1 - R) \tag{7}$$

For asymmetric bridging carbonyls $r_1 \neq r_2$ and D and R are independent geometric parameters for the Fe–C–Fe triangle, but for symmetric bridges $D = 0$, $R = 1.0$, and eq 7 cannot be used.

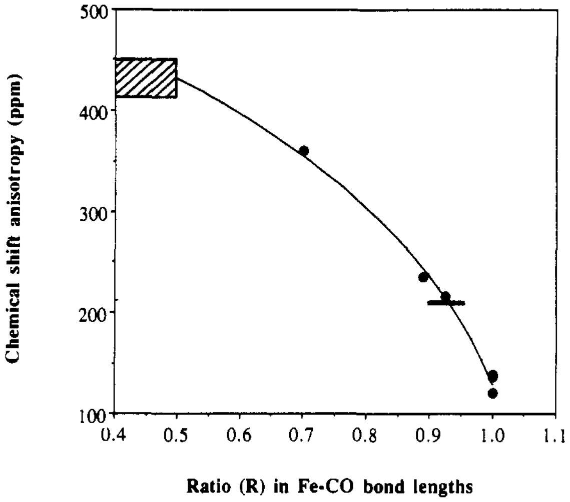

Figure 2. Plot of the ^{13}C chemical shift anisotropy ($\Delta\delta$) for the CO group vs the ratio (R) in Fe–CO bond lengths. Rms deviation between calculated curve (—) and experimental anisotropy = 7.5 ppm.

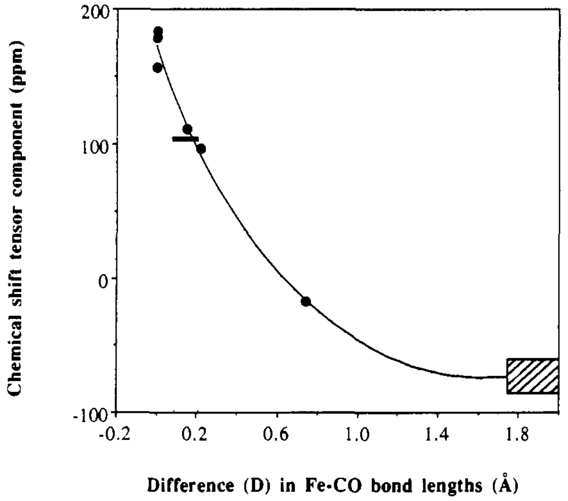

Figure 3. Plot of the lowest frequency chemical shift tensor component (δ_{33}) for the CO groups vs the difference (D) in Fe–CO bond lengths. Rms deviation between calculated curve (—) and experimental chemical shift = 7.6 ppm.

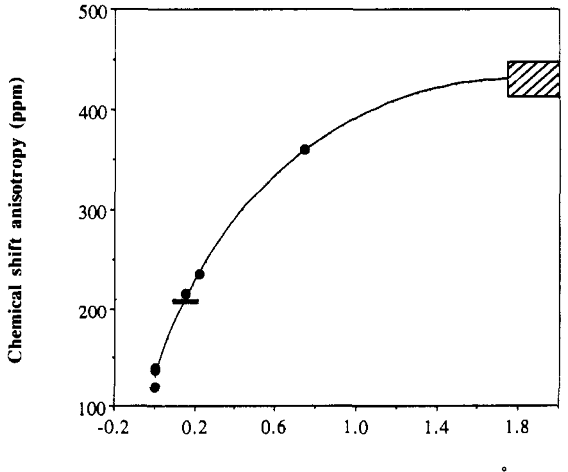

Figure 4. Plot of the ^{13}C chemical shift anisotropy ($\Delta\delta$) for the CO groups vs the difference (D) in Fe–CO bond lengths. Rms deviation between calculated curve (—) and experimental anisotropy = 6.4 ppm.

With this reservation in mind we compared the solid-state NMR data (δ_{iso}, δ_{11}, δ_{22}, δ_{33}, $\Delta\delta$, η) with D and R. We were able to include in these correlations a region corresponding to the terminal Fe–CO groups by noting that the second (nonbonded) iron to

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carbon distance is >3.5 Å from all of the published X-ray structural data on I–VI. The trial correlations involving the isotropic shieldings (δ_{iso}), the tensor components δ_{11} and δ_{22}, and the asymmetry parameters (η), are not good, but excellent correlations are obtained between δ_{33} and $\Delta\delta$ with R (Figures 1 and 2) and between δ_{33} and $\Delta\delta$ with D (Figures 3 and 4). In each of these correlations the horizontal bars that correspond to IV arise because of the uncertainty in the choice of the particular structural isomer and hence the appropriate values for r_1 and r_2. In each of these four cases (Figures 1–4) we made a least-squares fit of the data to a hyperbolic curve and the quality of the fits is such that we suggest that these curves may be used to find D and R and hence r_1 and r_2 (via eqs 6 and 7) for asymmetric bridging groups. It should be borne in mind that these carbonyl chemical shifts, while reflecting the degree of asymmetry of the bridge also include contributions from the nature and number of other substituents in the molecule and both intra- and intermolecular solid-state effects. However these additional contributions are likely to be relatively small, probably smaller than the spread in shielding values shown by the terminal ligands.

Conclusion

The slow MAS solid-state ^{13}C spectra of symmetrical double-bridging CO groups have the lowest frequency component of the chemical shift tensor in the region $\delta_{33} = 155–185$ ppm and the chemical shift anisotropy in the region $\Delta\delta = 120–140$ ppm. *Asymmetric* double-bridging and *terminal* CO groups have significantly lower frequency values for δ_{33} and much greater values for $\Delta\delta$. It has previously been reported[30] that the δ_{33} component for CO is quite invariant to the metal in the complexes $Ni(CO)_4$ and $Fe(CO)_5$ and in free CO. In contrast to this our results show that δ_{33} is the one component to give good correlation with the degree of bridging of the CO group. Furthermore, it is interesting to note that the value of δ_{33} is the least sensitive to errors in our application of the analysis of experimental data. This makes δ_{33} an even more valuable parameter. Similarly, $\Delta\delta$ (but not the asymmetry parameter, η) is a good indicator of the asymmetry in the CO group bridging. If our results are substantiated by further work, it may be possible to use derived δ_{33} and $\Delta\delta$ values to estimate the distances between the carbonyl carbon of an asymmetric bridging CO group and the iron atoms to which it is coordinated. This is an empirical correlation for which, as yet, we have no theoretical explanation. We are, however, investigating the quality of this type of correlation for the carbonyl complexes of the second- and third-row transition metals ruthenium and osmium.

Acknowledgment. The spectra of *cis*- and *trans*-I, II, IV, and V were measured by the University of London Intercollegiate Solid-State NMR Service (Bruker MSL-300) managed by Dr. C. J. Groombridge at Royal Holloway and Bedford New College.

Registry No. *cis*-I, 33221-55-5; *trans*-I, 32757-46-3; II, 76216-28-9; III, 57556-83-9; IV, 12101-59-6; V, 15321-51-4; VI, 17685-52-8.

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Formation of Carbonyl–Carbonate Complexes of Molybdenum by Reductive Disproportionation of Carbon Dioxide. X-ray Structure of $Mo_4(\mu_4\text{-}CO_3)(CO)_2(O)_2(\mu_2\text{-}O)_2(\mu_2\text{-}OH)_4(PMe_3)_6$

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The reaction of carbon dioxide with the bis(dinitrogen) complex *cis*-$Mo(N_2)_2(PMe_3)_4$, in coordinating solvents, gives the carbonyl–carbonate complexes $[Mo(\mu_2\text{-}\eta^1,\eta^2\text{-}CO_3)(CO)(PMe_3)_3]_2$ (**2**) and $Mo(CO_3)(CO)(PMe_3)_4$ (**3**) derived from the metal-induced reductive disproportionation of CO_2. The use of Et_2O or THF as the reaction solvent leads to the preferential formation of binuclear **2** whereas in acetone monomeric **3** is the preferred product. Compounds **2** and **3** interconvert readily by association or dissociation of PMe_3, and their solution stabilities have been found to be strongly solvent dependent. Interaction of **3** with the chelating phosphines dmpe or dmpm (dmpe = $Me_2PCH_2CH_2PMe_2$; dmpm = $Me_2PCH_2PMe_2$), under appropriate conditions, affords the related complexes $Mo(CO_3)(CO)(P\text{-}P)(PMe_3)_2$ (P-P = dmpe, **4**; P-P = dmpm, **5**) and $Mo(CO_3)(CO)(dmpe)_2$ (**6**). Compounds **2** and **3** react with H_2O with formation of an unusual tetrametallic, mixed-valence Mo(II)–Mo(V) complex $Mo_4(\mu_4\text{-}CO_3)(CO)_2(O)_2(\mu_2\text{-}O)_2(\mu_2\text{-}OH)_4(PMe_3)_6$ (**7**) that contains a unique carbonate ligand engaged in a novel type of bonding. The structure of **7** has been determined by X-ray crystallography. Crystals of **7** are orthorhombic, *Pbcn*, with unit cell constants $a = 26.866$ (9) Å, $b = 12.934$ (4) Å, $c = 11.965$ (2) Å, and $D(\text{calcd}) = 1.74$ g cm^{-3} for $Z = 4$.

Introduction

Studies on the chemical reactivity of electron-rich metal complexes have shown they are able to promote a number of interesting transformations of carbon dioxide.[2] A commonly observed reaction is oxygen transfer from CO_2 to another substrate. The latter could be for example an oxophilic metal center[3,4] or a readily oxidized ligand, frequently a phosphine ligand.[5] In some other cases, oxygen transfer from one molecule of CO_2 to another is observed, and in fact, a common reaction experienced by CO_2, when exposed to strongly reducing metal systems, is its reductive disproportionation[6a] to CO_3^{2-} and CO (eq 1). This transformation,

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