Table I. Activation and Dnmr Parameters for *tert*-Butyl Rotation in *tert*-$C_4H_9(C_6H_5)_2PM(CO)_5$ Complexes

| Compd | Slow-exchange *tert*-butyl dnmr parameters | | $\Delta H^{\ddagger}$, kcal/mol | $\Delta S^{\ddagger}$, gibbs | $\Delta G^{\ddagger}$, kcal/mol (temp, °C) |
	δ,^{a} ppm	$^3J_{PCCH}$, Hz			
tert-$C_4H_9(C_6H_5)_2PCr(CO)_5$	1.36 (6 H)	16.5 ± 0.5			8.4 ± 0.2 (−109.8)
	1.22 (3 H)	10.0 ± 0.5			
tert-$C_4H_9(C_6H_5)_2PMo(CO)_5$	1.33 (6 H)	17.8 ± 0.5			8.3 ± 0.2 (−110.0)
	1.25 (3 H)	10.2 ± 0.5			
tert-$C_4H_9(C_6H_5)_2PW(CO)_5$	1.36 (6 H)	17.5 ± 0.5	8.7 ± 0.6	2 ± 6	8.3 ± 0.2 (−113.7)
	1.28 (3 H)	10.0 ± 0.5			

^{a} Downfield from tetramethylsilane.

**Table II.** Activation Parameters for *tert*-Butyl Rotation in Selected *tert*-Butylphosphines

Compd	$\Delta H^{\ddagger}$ kcal/mol	$\Delta S^{\ddagger}$ gibbs	$\Delta G^{\ddagger}$, kcal/mol (temp, °C)
$(tert$-$C_4H_9)_3P$	9.0 ± 0.4^a	2 ± 4	8.6 ± 0.1 (−103)
$(tert$-$C_4H_9)_3PS$	9.5 ± 0.4^a	−5 ± 4	10.5 ± 0.1 (−72)
$(tert$-$C_4H_9)_3PBH_3$	10.0 ± 0.2^b	−2 ± 2	10.4 ± 0.1 (−68)
$(tert$-$C_4H_9)_2ClPBH_3$	7.0 ± 0.4^b	0 ± 5	6.8 ± 0.1 (−141)
tert-$C_4H_9(C_6H_5)_2PW(CO)_5$	8.7 ± 0.6^c	2 ± 6	8.3 ± 0.2 (−114)
tert-$C_4H_9(CH_3)_2NBH_3$	11.2 ± 0.3^d	6 ± 2	10.0 ± 0.1 (−79)

^{a} See ref 2a. ^{b} See ref 3. ^{c} This work. ^{d} C. H. Bushweller, W. J. Dewkett, J. W. O'Neil, and H. Beall, *J. Org. Chem.*, **36**, 3782 (1971).

Very similar changes were observed for the chromium (**1**) and molybdenum (**2**) analogs of **3**. Slow-exchange *tert*-butyl chemical shifts and free energies of activation ($\Delta G^{\ddagger}$) for *tert*-butyl rotation are listed in Table I.

In light of other available data concerning rotation about the C–P bond in various *tert*-butylphosphines,[2,3] a comparison of the free energies of activation ($\Delta G^{\ddagger}$) for *tert*-butyl rotation in **1–3** (Table I) reveals a remarkable insensitivity to variation of the metal pentacarbonyl moiety. However, in light of X-ray crystallographic data for $Cr(CO)_6$, $Mo(CO)_6$, and W-$(CO)_6$ revealing very similar metal covalent radii [Cr(1.48 ± 0.01 Å), Mo (1.62 ± 0.01 Å)][6] and metal–carbon bond lengths [Cr–C (1.92 ± 0.04 Å), Mo–C (2.08 ± 0.04 Å), W–C (2.06 ± 0.04 Å)][7] and similar Cr–P [2.422 Å in $(C_6H_5)_3P$-$Cr(CO)_5$][8] and Mo–P bond lengths [2.517 Å in $(C_6H_5)_2C_6$-$H_4CH=CHCH_3PMo(CO)_4$],[9] it is not surprising that the three metal pentacarbonyl groups have the same effective steric size in the context of hindering *tert*-butyl rotation.

Obtaining ^1H dnmr spectra for **1–3** under conditions of slow *tert*-butyl rotation (*e.g.*, Figure 1, −128.7°) also unveiled a significant dependence of $^3J_{PCCH}$ on molecular geometry. $^3J_{PCCH}$ for the methyl group trans to the metal in **1–3** (~10 Hz) is significantly smaller than that for the two methyls gauche to the metal (~17 Hz), *e.g.*, **4**. This

4
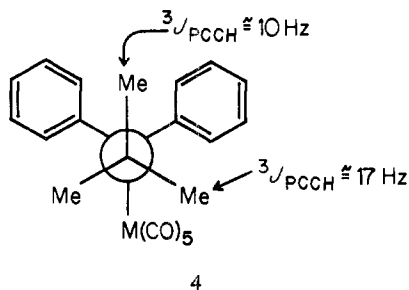
situation is similar to that in uncomplexed *tert*-butylphos-

phines[2] and *tert*-butylphosphine-boranes[3] and may prove to be a useful probe into free phosphine and complexed phosphine stereochemistry.

Only a limited amount of data is available concerning the dynamics of carbon–phosphorus single-bond rotation and only a qualitative picture of the effective hindering potential associated with a given substituent may be deduced. Indeed, a direct comparison between the free *tert*-butyldiphenylphosphine and complexes **1–3** is not possible because no *tert*-butyl dnmr peak separation was observed in the free phosphine.[2a] However, for purposes of comparison, activation parameters for *tert*-butyl rotation in selected free and complexed *tert*-butylphosphines as well as an amine–borane are compiled in Table II.

Experimental Section

The ^1H dnmr spectra were obtained using a Varian HR-60A spectrometer equipped with a custom-built variable-temperature probe.[10]

Complexes **1–3** were prepared according to the procedure of Grim and coworkers.[11]

Registry No. **1**, 18497-57-9; **2**, 18534-32-2; **3**, 18534-40-2.

(6) F. A. Cotton and D. C. Richardson, *Inorg. Chem.*, **5**, 1851 (1966).

(7) L. O. Brockway, R. V. G. Ewens, and M. W. Lister, *Trans. Faraday Soc.*, **34**, 1350 (1938).

(8) H. J. Plastos, J. M. Stewart, and S. O. Grim, *J. Amer. Chem. Soc.*, **91**, 4326 (1969).

(9) H. Luth, M. R. Truter, and A. Robson, *J. Chem. Soc. A*, **28** (1969).

(10) F. R. Jensen, L. A. Smith, C. H. Bushweller, and B. H. Beck, *Rev. Sci. Instrum.*, **43**, 894 (1972).

(11) S. O. Grim, D. A. Wheatland, and W. McFarlane, *J. Amer. Chem. Soc.*, **89**, 5573 (1967).

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Magnetic Field Mossbauer Spectroscopy of Metal Cluster Systems. $[(\pi$-$C_5H_5)Fe(CO)]_4$ and $[(\pi$-$C_5H_5)Fe(CO)]_4^+$

R. B. Frankel,* W. M. Reiff, T. J. Meyer, and J. L. Cramer

We report the use of Mossbauer spectroscopy in external magnetic fields to study certain features of the electronic structure of the tetrahedral metal–metal bonded clusters $[(\pi$-$C_5H_5)Fe(CO)]_4$ and $[(\pi$-$C_5H_5)Fe(CO)]_4^+$ (Figure 1). Specifically, we are interested in ascertaining whether the unpaired electron in the paramagnetic monocation is localized on the iron sites or is extensively delocalized to the ligands. The question is relevent because in certain iron–sulfur proteins, the electrons involved in the oxidation and re-

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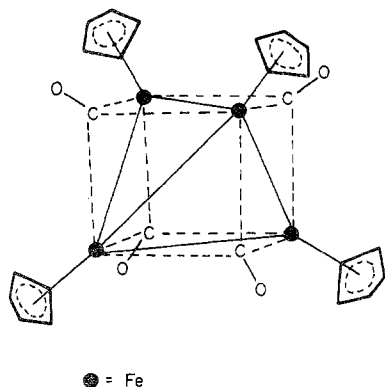
Figure 1. Structure of the $[(\pi\text{-}C_5H_5)Fe(CO)]_4$ cluster unit.

Figure 2. Mossbauer spectra of (a) $[(\pi\text{-}C_5H_5)Fe(CO)]_4$ and (b) $[(\pi\text{-}C_5H_5)Fe(CO)]_4{}^+(PF_6)^-$ at 4.2 K in a longitudinal magnetic field of $H_0 = 80$ kOe. The solid lines are computer-calculated spectra with the parameters (a) $\Delta E_Q = 1.76$ mm/sec, $H_n = 80$ kOe and (b) $\Delta E_Q = 1.38$ mm/sec, $H_n = 70$ kOe.

duction steps interact strongly with the Fe–S "core."[1] On the other hand, the electrons involved in the various oxidation processes of certain iron–sulfur–dithiolene complexes which are related structually to $[(\pi\text{-}C_5H_5)Fe(CO)]_4$ appear to be extensively delocalized and do not interact with the Fe–S "core."[2] A related question of considerable interest is the site of oxidation in compounds containing strong metal–metal bonds.

Ferguson and Meyer[3] found that the $[(\pi\text{-}C_5H_5)Fe(CO)]_4$ cluster unit, first prepared by King,[4] can exist in 2+, 1+, 0, and 1− oxidation states. Of these the 0 and 1+ clusters can be isolated as solids and the monocation has been obtained as both halide and $PF_6{}^-$ salts. The magnetic susceptibilities of $[(\pi\text{-}C_5H_5)Fe(CO)]_4$ and $[(\pi\text{-}C_5H_5)Fe(CO)]_4(PF_6)$ have been measured.[3] The neutral cluster is diamagnetic while the monocation is paramagnetic with a temperature-dependent moment (e.g., $\mu_{eff} = 2.46$ μ_B at 295 K and $\mu_{eff} = 1.77$ μ_B at 4.2 K).[5]

Mossbauer experiments at 77 K in zero magnetic field were reported by Greatrex and Greenwood,[6] who found single pairs of quadrupole-split lines with isomer shifts $\delta = 0.66$ mm/sec and $\delta = 0.67$ mm/sec (relative to ^{52}Co in Pd) and quadrupole splittings $\Delta E_Q = 1.76$ mm/sec and $\Delta E_Q = 1.40$ mm/sec for the neutral molecule and the monocation, respectively. They suggested two alternative explanations for why δ did not change upon oxidation: (i) the electron is removed from ligand-based orbitals; (ii) the electron is removed from orbitals including the iron atoms, but a compensating set of changes leaves the electron density at the nucleus unchanged. In either case, all the irons are apparently equally affected, because only one quadrupole doublet is observed in each case.[6]

Our experiment was designed to test the two alternatives suggested by Greatrex and Greenwood. Application of a large magnetic field at low temperature will polarize the unpaired spin in the paramagnetic monocation. If this unpaired spin interacts strongly with the iron sites, then we expect to see a resultant magnetic hyperfine interaction, in addition to the direct interaction of the nuclear moment with the applied field. If the unpaired electron is predominantly ligand based, we expect no additional magnetic
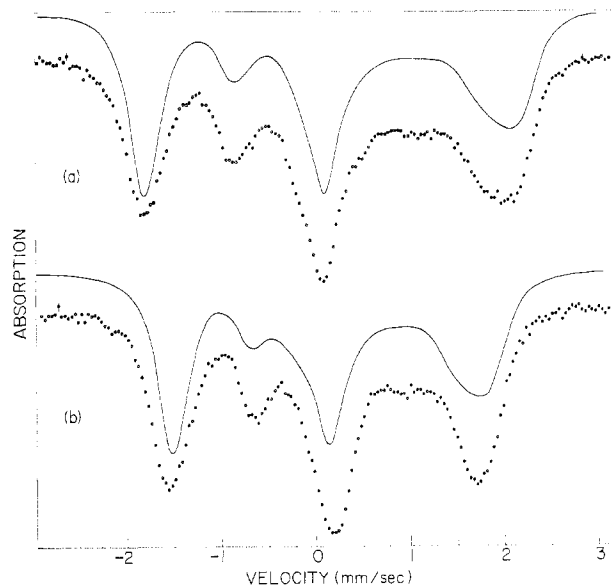
hyperfine splitting, as was observed in dithiolene–metal cluster complexes.[2]

The measurements were made with a conventional constant-acceleration Mossbauer spectrometer, and the fields were generated by a Nb_3Sn superconducting magnet operating in the persistent mode up to 80 kOe. The polarization direction was longitudinal, and both source and absorber were held at 4.2 K. The monocation was obtained as the $PF_6{}^-$ salt.

The spectra at 80 kOe are plotted in Figure 2. The solid lines are computer-generated spectra for fields applied to the randomly oriented powder and using the values of the quadrupole splitting measured in zero field at 4.2: $\Delta E_Q = 1.76$ mm/sec and $\Delta E_Q = 1.38$ mm/sec for the neutral molecule and monocation, respectively. For the neutral molecule the calculated spectrum with the total field at the nucleus $H_n = 80$ kOe satisfactorily represents the experimental spectrum, but for the monocation a satisfactory representation requires $H_n = 70$ kOe, i.e., 10 kOe less than H_0 and well outside of experimental error (±2 kOe). In both cases, the sign of the principal component of the electric field gradient tensor is positive and the asymmetry parameter is small. For $H_0 < 30$ kOe, it is not possible to measure H_n. Nevertheless, it is clear that in the neutral molecule $H_n = H_0$ over the entire range of field (Figure 3), while in the monocation there is an additional hyperfine interaction of ~ 10 kOe and of negative sign. The field dependence is constant above $H_0 = 30$ kOe. For free-spin behavior one expects a Brillouin function dependence of the hyperfine field on external field and temperature. This would be close to saturated by $H_0 = 30$ kOe at 4.2 K. If the electronic relaxation time is long compared to the Larmor precession time, then the saturation hyperfine field would be obtained even for $H_0 < 30$ kOe.

We interpret this result as showing that the unpaired electron does interact with the iron sites in the metal–metal bonded "core" of the cluster and that all the iron sites are equivalent. The magnitude of the hyperfine interaction is relatively small, compared, for example, with the hyperfine fields observed in the iron–sulfur proteins. Rao, et al.,[7] observed hyperfine fields of −370 and ~−200 kOe for the

(1) J. C. M. Tsibris and R. W. Woody, *Coord. Chem. Rev.*, 5, 417 (1970).

(2) R. B. Frankel, W. M. Reiff, I. Bernal, and M. Good, *Inorg. Chem.*, 13, 493 (1974).

(3) J. A. Ferguson and T. J. Meyer, *J. Amer. Chem. Soc.*, 94, 3409 (1972).

(4) R. B. King, *Inorg. Chem.*, 5, 2227 (1966).

(5) G. W. Inman, W. E. Hatfield, and T. J. Meyer, unpublished results.

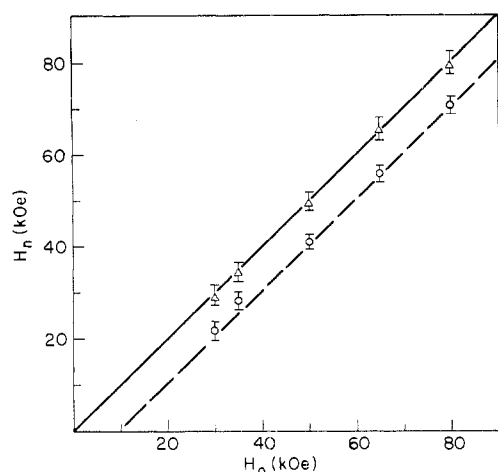(6) P. Greatrex and N. N. Greenwood, *Discuss. Faraday Soc.*, 47, 126 (1969).

Figure 3. Total field at the nucleus H_n plotted as a function of external field H_0: triangles, $[(\pi\text{-}C_5H_5)Fe(CO)]_4$; circles, $[(\pi\text{-}C_5H_5)Fe\text{-}(CO)]_4{}^+(PF_6)^-$.

oxidized and reduced forms of the one-iron protein rubredoxin, respectively. Dunham, *et al.*,[8] and Rao, *et al.*,[9] observed hyperfine fields of $\sim\!-180$ kOe for each of the two sites in the reduced two-iron ferredoxins. In the oxidized form of the four-iron high-potential iron protein from *Chromatium*, Evans, *et al.*,[10] reported hyperfine fields of 121 and 90 kOe. However, direct comparisions between the results obtained in the proteins and the results reported here are not very meaningful because the oxidation states of the iron sites in the present complexes are not known and may not correspond to those in the proteins. Moreover, it is not presently possible to make a quantitiative estimate of the extent of spin delocalization onto the ligands because there are no data or theoretical estimates which give the hyperfine coupling constant per spin in chemical systems of this kind.

The experimental results are consistent with a model for $[(\pi\text{-}C_5H_5)Fe(CO)]_4{}^+$ in which the unpaired electron occupies a delocalized MO at least partly and perhaps largely metal-metal bonding in character. The results agree with a qualitative MO model presented by Toan, Felhammer, and Dahl[11] in conjunction with their crystallographic studies on the $[(\pi\text{-}C_5H_5)Fe(CO)]_4$ and $[(\pi\text{-}C_5H_5)Fe(CO)]_4(PF_6)$ cluster systems. According to this model the highest filled MO's are $e + t_1 + t_2$, formed by appropriate symmetry combinations of iron 3d orbitals. The $e + t_1 + t_2$ orbitals are largely nonbonding with the highest one somewhat antibonding with respect to the metal atoms. In this model, oxidation of $[(\pi\text{-}C_5H_5)Fe(CO)]_4$ to $[(\pi\text{-}C_5H_5)Fe(CO)]_4{}^+$ occurs by loss of an electron from one of the set of nonbonding orbitals giving the configuration $(e + t_1 + t_2)$.[11] Some spin delocalization onto the carbonyl ligands is expected in this model since the nonbonding $e + t_1 + t_2$ levels are stablized by metal–carbonyl back-bonding.

It is of interest to note that our previous study on the structurally related cluster system $[Fe_4S_4\{S_2C_2(CF_3)_2\}]_4{}^-$

(7) K. K. Rao, M. C. W. Evans, R. Cammack, D. O. Hall, C. L. Thompson, P. J. Jackson, and C. E. Johnson, *Biochem. J.*, 129, 1063 (1972).
(8) W. R. Dunham, A. J. Bearden, I. T. Salmeen, G. Palmer, R. H. Sands, W. H. Orme-Johnson, and H. Beinert, *Biochim. Biophys. Acta*, 253, 134 (1971).
(9) K. K. Rao, R. Cammack, D. O. Hall, and C. E. Johnson, *Biochem. J.*, 122, 257 (1971).
(10) M. C. W. Evans, D. O. Hall, and C. E. Johnson, *Biochem. J.*, 119, 289 (1970).
(11) Trinh-Toan, W. P. Felhammer, and L. P. Dahl, *J. Amer. Chem. Soc.*, 94, 3389 (1972).

showed essentially no hyperfine interaction. In the singly reduced dithiolate cluster, in which the sulfurs rather than CO groups bridge the iron atoms, the absence of a measurable hyperfine interaction may indicate extensive delocalization onto the ligands. As a consequence the redox properties of the dithiolate cluster may be carried, at least in part, by ligand-based orbitals. Hopefully, work currently in progress on the structurally related clusters $[(\pi\text{-}C_5H_5)FeS]_4$, $[(\pi\text{-}C_5H_5)FeS]_4(PF_6)$, and $[(\pi\text{-}C_5H_5)FeS]_4(PF_6)_2$ will help further to elucidate the electronic structure of these systems.

Electron Paramagnetic Resonance and Electronic Spectral Evidence for Isomers Resulting from Basal and Axial Ligation of Bis(hexafluoroacetylacetonato)copper(II) by Triphenylphosphine

B. B. Wayland* and V. K. Kapur

Bis(β-diketonato)copper(II) complexes form a wide variety of five-coordinate 1:1 adducts with neutral donor molecules.[1-14] In many cases the neutral donor occupies the axial position of an idealized square pyramid.[5,6] Epr studies of the mono(pyridine) adduct of bis(hexafluoroacetylacetonato)copper(II) $[Cu(Hfacac)_2]$ lead to the proposal that pyridine occupies a basal position in a square pyramid.[7] An X-ray structure determination has proven the occurrence of this type of structure in the 4-aminopyridine adduct of bis(acetylacetonato)copper(II).[8] Pradilla-Sorzano and Fackler have recently reported that $Cu(Hfacac)_2\cdot H_2O$ diluted into

(1) D. P. Graddon, *Coord. Chem. Rev.*, 4, 1 (1969).
(2) B. L. Libutti, B. B. Wayland, and A. F. Garito, *Inorg. Chem.*, 8, 1510 (1969).
(3) W. Partenheimer and R. S. Drago, *Inorg. Chem.*, 9, 47 (1970).
(4) C. H. Ke, R. J. Kurland, C. I. Lin, and N. C. Li, *J. Phys. Chem.*, 74, 1728 (1970).
(5) H. Yokoi, M. Sai, and T. Isobe, *Bull. Chem. Soc. Jap.*, 42, 2232 (1969).
(6) S. Ooi and Q. Fernando, *Chem. Commun.*, 532 (1971).
(7) B. B. Wayland and M. D. Wisniewski, *Chem. Commun.*, 1025 (1971).
(8) G. W. Bushnell, *Can. J. Chem.*, 49, 555 (1971).
(9) J. Pradilla-Sorzano and J. P. Fackler, Jr., *Inorg. Chem.*, 13, 38 (1974).
(10) R. A. Zelonka and M. C. Baird, *Can. J. Chem.*, 50, 1269 (1972).
(11) F. Leh and K. M. Chan, *Bull. Chem. Soc. Jap.*, 45, 2709 (1972).
(12) M. D. Wisniewski, Ph.D. Thesis, University of Pennsylvania, 1973.
(13) J. A. Bertrand and R. L. Kaplan, *Inorg. Chem.*, 5, 489 (1966).
(14) B. J. Hathaway and A. A. G. Tomlinson, *Coord. Chem. Rev.*, 5, 1 (1970); B. M. Hathaway and D. E. Billing, *ibid.*, 5, 143 (1970).