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Bonding of Molecular Nitrogen in *trans*-Hydrido(dinitrogen)bis(phosphine)iron(II) Tetraphenylborate. A Mössbauer Study

Sir:

We have previously reported the preparation and some spectroscopic properties of cationic compounds of the general formula *trans*-$[MH(L)(depe)_2]^+BPh_4^-$ (M = Fe, Ru, Os; L = CO, p-MeO·C_6H_4·NC, Me_3CNC, $P(OPh)_3$, $P(OMe)_3$, N_2, PhCN, and MeCN).[1,2] Mössbauer center shifts[2] indicated that the σ donor plus π acceptor ability ($\sigma + \pi$) increased in the order MeCN < PhCN $\sim$ N_2 < $P(OPh)_3$ $\sim$ $P(OMe)_3$ < Me_3CNC < p-MeO·C_6H_4·NC < CO. Thus N_2 is a much weaker ($\sigma + \pi$) ligand than CO or RNC, but comparable to PhCN and slightly stronger than MeCN.

Table I. Room Temperature Quadrupole Splittings for *trans*-$[FeH(L)(depe)_2]^+BPh_4^-$ Complexes

No.	L	QS
1	CO	(−)1.00
2	p-$MeOC_6H_4NC$	−1.14
3	Me_3CNC	(−)1.13
4	$P(OMe)_3$	(−)0.90
5	$P(OPh)_3$	(−)0.72
6	N_2	(−)0.33
7	PhCN	(−)0.58
8	MeCN	(−)0.46

The variations in quadrupole splittings (Table I), which can also be related to bonding properties,[3] were not discussed previously because the signs of the quadrupole splittings were not known. The determination of the sign of one of these compounds (compound **2**) makes it possible to separate, at least qualitatively, the relative σ and π characteristics of N_2 relative to those of the other neutral ligands. The sign of the QS for the N_2 complex could not be determined directly by the magnetic field technique because of its very small QS. However, the sign can be safely assumed (*vide infra*) after the sign for one of these compounds is determined.

A typical spectrum of compound **2** in an applied longitudinal magnetic field of 28 kG at 4.2°K is shown in Figure 1. As discussed by Collins,[4] the two-line zero-field spectrum splits into a doublet and a triplet in a magnetic field. If the doublet is at positive velocities, the signs of V_{zz} and the quadrupole splitting are positive; if the doublet is at negative velocities, the sign of V_{zz} is negative. Figure 1 shows clearly that the doublet is at negative velocities, and the sign of V_{zz} is negative. This spectrum shows considerable deviation from that theoretically expected. This deviation is probably due either to preferred orientation effects or the Goldanskii–Karyagin effect.

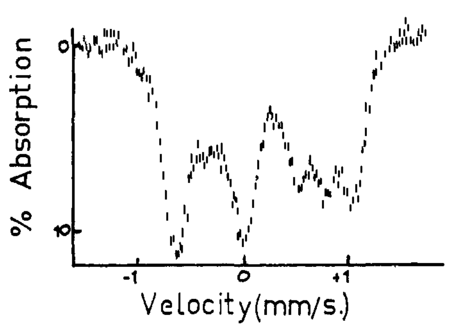

Figure 1. Mössbauer spectrum of compound **2** at 4°K in an applied magnetic field of 28 kG.

The magnitude and sign of the quadrupole splitting for compound **2** is in good agreement with that expected from previously derived partial quadrupole splitting (PQS) values. Taking the PQS values of H^- to be −1.04, RNC = −0.69, and depe/2 = −0.62,[5] the predicted QS for compound **2** is −0.98 mm/sec compared with the observed −1.14 mm/sec. The predicted values for the phosphite compounds from derived PQS values[6] are also negative in sign, and the magnitudes are again in good agreement with the observed values. In addition, the range of PQS values observed for a large number of neutral ligands (−0.40 to −0.70)[6] gives an expected range of values for any *trans*-$FeHL(depe)_2^+$ species of −0.40 to −1.00 mm/sec. It is safe to assume then that all quadrupole splittings reported in Table I are negative.

The QS becomes more positive as the π acceptor function of L increases and more negative as the σ donor function of L increases, *i.e.*, QS $\propto$ ($\pi - \sigma$).[3] π acceptance withdraws d electron density along the Z EFG direction (from d_{XZ} and d_{YZ}), whereas σ donation increases the d electron density along the Z EFG direction (to d_{Z^2} and p_Z).

The molecular nitrogen compound has the most positive QS, indicating that it is the best ($\pi - \sigma$) ligand. By contrast, as noted earlier, the center shifts indicate that it is one of the poorest ($\sigma + \pi$) ligands. These results show that, relative to CO, N_2 is a much poorer ($\sigma + \pi$) ligand, but that π acceptance relative to σ donation is more important in N_2 than in CO. Or to compare N_2 with RCN ligands, the CS and QS data indicate that N_2 is a better π acceptor but a poorer σ donor than RCN. Relatively then, N_2 is a moderate π acceptor but a weak σ donor. This result is consistent with the conclusion presented previously[7] which

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(1) G. M. Bancroft, M. J. Mays, and B. E. Prater, *Chem. Commun.*, 585 (1969).

(2) G. M. Bancroft, M. J. Mays, B. E. Prater, and F. P. Stefanini, *J. Chem. Soc. A*, 2146 (1970).

(3) G. M. Bancroft, M. J. Mays, and B. E. Prater, *ibid.*, *A*, 956 (1970).

(4) R. L. Collins, *J. Chem. Phys.*, **42**, 1072 (1965).

(5) The signs of the QS chosen in ref 3 were incorrect [G. M. Bancroft, R. E. B. Garrod, A. G. Maddock, M. J. Mays, and B. E. Prater, *Chem. Commun.*, 200 (1970)] making the PQS values in Table II of ref 3 reversed about the value for Cl^-. The effect of the different signs is discussed.[3] The correct values for depe, H, and RNC[6] are obtained simply by inverting the values given in Table II about −0.30.

(6) G. M. Bancroft, R. E. B. Garrod, and A. G. Maddock, *J. Chem. Soc. A*, 3165 (1971); G. M. Bancroft and E. T. Libbey, unpublished observations.

(7) J. Chatt, D. P. Melville, and R. L. Richards, *J. Chem. Soc. A*, 2841 (1969).

indicated that the instability of N_2 compounds is associated mostly with the weak σ donor properties of that ligand.

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Hyperconjugative and p–d Homoconjugative Effects of Silicon, Germanium, and Tin on Alkyl Radicals from Electron Spin Resonance Studies

Sir:

The exceptional stabilization of neighboring carbonium-ion centers by metal substituents including Si and Sn of group IVb has been ascribed to hyperconjugative electron release from the carbon–metal bonds.[1] The enhanced reactivity of allylsilanes to free-radical addition[2] can also be attributed to the stabilization of the organometallic radical. Indeed, previous studies[3] have shown that alkyl radicals with β-S, Si, Ge, and Sn substituents exist in a preferred conformational orientation in which the metal substituent (R_3M) occupies an eclipsed position relative to the half-filled carbon p orbital and optimally located to interact with it. The magnitude of this interaction can be as large as 5 kcal/mol.[4]

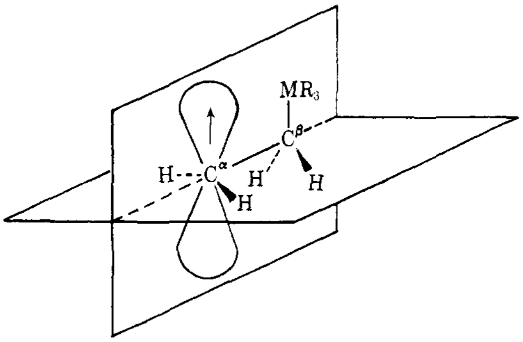

Table I. Esr Parameters of $(CH_3)_3MCH_2\dot{C}H_2$[a]

M	T, °C	$a(H_\alpha)$	$a(H_\beta)$	$a(CH_3)$	M	a(M)	$\langle g\rangle^b$ iso	$da(H_\beta)/dT$
C	−105	22.06	24.71	0.1			2.00268	0.002
Si	−112	21.05	17.68	0.10	^{29}Si	37.4[c]	2.00265	0.013
Ge	−100	20.70	16.57	0.14			2.00255	0.0075
Sn	−101	19.69	15.84	0.15	^{119}Sn	488.9[b]	2.00205	0.0067
					^{117}Sn	467.7[b]		

[a] Isotropic coupling constants in gauss. [b] Corrected to second order with respect to hyperfine interactions. [c] Value for $Et_3SiCH_2\dot{C}H_2\cdot$ at −148°.[3a]

In this report we wish to probe the mechanism of this interaction by examining the electron spin resonance (esr) parameters obtained from the spectra of the organometallic radicals listed in Table I. The radicals were generated in solution by adding the metal-centered radical [$R_3M\cdot$ = $(CH_3)_3Si\cdot$, $(CH_3)_3Ge\cdot$, $(CH_3)_3Sn\cdot$] to ethylene[3] or by metathesis between 3,3-dimethylbutyl chloride and triethylsilyl radical.[5]

Values of the β-proton coupling constant (a_{H_β}) lower than that of the ethyl radical (26.87 G)[6] and their positive temperature dependence show that the stable conformation of the Si-, Ge-, and Sn-substituted ethyl radicals has the C_β–M bond eclipsing the p orbital on the radical center.[3b]

Two features of the esr parameters listed in Table I are noteworthy. First, the isotropic g factors of the β-metal substituted ethyl radicals decrease with increasing atomic number of M, and the drop is especially pronounced with Sn. In contrast, the g factors of the metal-centered radicals, in which the odd electron occupies mainly a valence-shell p orbital, increases as the atomic number of the metal increases: $g[CH_3\cdot] = 2.00255$,[6] $g[(CH_3)_3Si\cdot] = 2.0031$,[7] $g[H_3Si\cdot] = 2.0032$,[7] $g[(CH_3)_3Ge\cdot] = 2.01003$,[8] $g[H_3Ge\cdot] = 2.012$,[9] and $g[H_3Sn\cdot] = 2.018$.[9] Moreover, the g factors of α-metal substituted methyl radicals, in which the odd-electron orbital around the metal is mainly its valence-shell d orbital, decrease as the atomic number of the metal increases:[10] $g[(CH_3)_3CCH_2\cdot] = 2.0026$, $g[(CH_3)_3SiCH_2\cdot] = 2.0025$, $g[(CH_3)_3GeCH_2\cdot] = 2.0023$, $g[(CH_3)_3SnCH_2\cdot] = 2.0008$. The observed trend of the g factors for β-substituted ethyl radicals is, thus, consistent with the delocalization of the odd electron onto vacant d orbitals of the metal.

The second feature of these β-substituted ethyl radicals is the large hyperfine splittings by the metal. The spectrum of $(CH_3)_3SnCH_2CH_2\cdot$ in Figure 1, for example, shows the large splittings by ^{117}Sn and ^{119}Sn in natural abundance. The metal coupling constants increase with the atomic number of M and are significantly larger than those observed with the corre-

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(1) (a) W. Hanstein, H. J. Berwin, and T. G. Traylor, *J. Amer. Chem. Soc.*, **92**, 829, 7476 (1970); J. H. Jerkunica and T. G. Traylor, *ibid.*, **93**, 6278 (1971); (b) B. E. Cooper and W. J. Owen, *J. Organometal. Chem.*, **29**, 33 (1971).

(2) (a) H. Sakurai, A. Hosomi, and M. Kumada, *J. Org. Chem.*, **34**, 1764 (1969). (b) The increased reactivity of allylsilanes compared to vinylsilanes has also been noted in copolymerization studies (C. C. Price and T. Yukuta, private communication). (c) Also *cf.* R. A. Jackson, *Advan. Free-Radical Chem.*, **3**, 231 (1969).

(3) (a) P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, **91**, 6161 (1969); (b) *ibid.*, **93**, 846 (1971).

(4) T. Kawamura and J. K. Kochi, *J. Organometal. Chem.*, **30**, C8 (1971).

(5) *Cf.* A. Hudson and R. A. Jackson, *Chem. Commun.*, 1327 (1969).

(6) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

(7) S. W. Bennett, C. Eaborn, A. Hudson, R. A. Jackson, and K. D. J. Root, *J. Chem. Soc. A*, 348 (1970).

(8) T. Kawamura and J. K. Kochi, unpublished results.

(9) R. L. Morehouse, J. J. Christiansen, and W. Gordy, *J. Chem. Phys.*, **45**, 1751 (1966).

(10) J. H. Mackey and D. E. Wood, *Mol. Phys.*, **18**, 783 (1970). In the analysis of the d-orbital contributions to the g factors these authors used the spin–orbit coupling constants of p orbitals for positive ions (Si, 190 cm^{-1}; Ge, 1200 cm^{-1}; Sn, 2800 cm^{-1}) instead of those of d orbitals (Si, 5 cm^{-1}; Ge, 60 cm^{-1}; Sn, 240 cm^{-1}): private communication. Thus the evaluated odd-electron densities on the d orbitals were underestimated about a factor of 10.