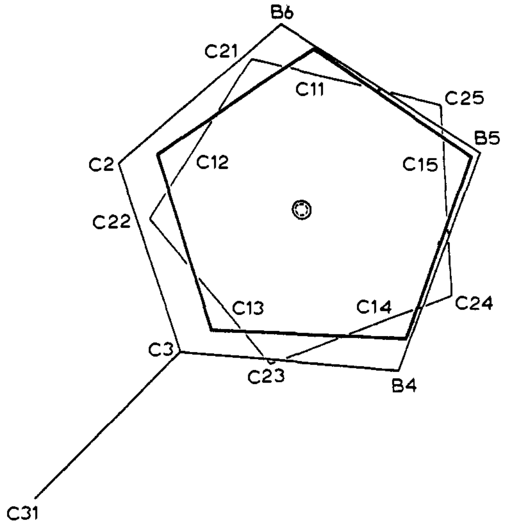

Figure 2. A view down the Co–Co bond in III, illustrating the crystal orientation of the three rings. The carbon atoms C11–C15 form the top ring and the carbons C21–C25 the bottom ring. The methyl group (C31) is only −0.008 Å from the plane of the C_2B_3 ring.

C25) ring is almost completely staggered relative to the other two rings. While the orientation of the C_5H_5 rings in metallocenes is still a subject of controversy, recent data suggest that in general the eclipsed configuration is the more stable. The presence of both eclipsed and staggered arrangements in III indicates that the factors determining the relative orientation of planar π-type rings may be more complex than anticipated. With the Co atoms situated 1.568 and 1.572 Å from the C_2B_3 plane all other distances are relatively normal.

The stability of the triple-decked compounds I–III is of interest in view of the scarcity of corresponding cyclopentadienyl species. Peaks attributed to $M_2(C_5H_5)_3^+$ ions, for which triple-decked structures were suggested, have been observed in the mass spectra of ferrocene and nickelocene[6] but structural data are lacking. The recently reported[7] $Ni_2(C_5H_5)_3^+$ system, for which a triple-decked structure has been proposed from nmr and ir data, is converted to nickelocene by water and other solvents; in contrast, compounds I–III are unreactive to water and air. Ligand–metal bonding in metallocarboranes has been discussed elsewhere,[1] but the situation in complexes I–III appears novel with respect to the simultaneous bonding of both faces of the central ring to metal atoms. The new complexes may be qualitatively similar to the pentagonal bipyramidal species $B_7H_7^{2-}$, $C_2B_5H_7$, and $CH_3GaC_2B_4H_6$, which have been described[8,9] in terms of delocalized π_{p_z} molecular orbitals on the ring combined with orbitals of appropriate symmetry on the apex atoms,[8] resulting in a set of filled bonding molecular orbitals for the cage system.

While it appears improbable that a free $C_2B_3H_5^{4-}$ ion would be stable, the chemistry of this ring system and its diprotonated form $C_2B_3H_7^{2-}$ in metal complexes is expected to be large in scope and may extend to unprecedented multiple-decked stacked compounds incorporating several metal atoms sandwiched between alternating carborane rings. We are presently examining such structural possibilities.

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(6) E. Schumacher and R. Taubenest, *Helv. Chim. Acta*, **47**, 1525 (1964).

(7) A. Salzer and H. Werner, *Angew. Chem., Int. Ed. Engl.*, **11**, 930 (1972); *Syn. Inorg. Metal-Org. Chem.* **2**, 239 (1972).

(8) (a) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 2179 (1962); (b) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963; (c) W. N. Lipscomb, *Proc. Nat. Acad. Sci. U. S.*, **47**, 1791 (1961).

(9) R. N. Grimes, W. J. Rademaker, M. L. Denniston, R. F. Bryan, and P. T. Greene, *J. Amer. Chem. Soc.*, **94**, 1865 (1972).

Mössbauer Study of Stereochemistry Intermediate to Octahedral and Trigonal Prismatic

Sir:

The difficulty in distinguishing octahedral or trigonal antiprismatic (TAP) from trigonal prismatic (TP) coordination with conventional techniques (electronic spectra, nmr, magnetic susceptibility, etc.) is emphasized in low-spin iron(II) complexes. Such materials typically exhibit small, temperature-independent magnetic moments that are uninformative relative to variation in stereochemistry. The types of ligands capable of resulting in spin paired d^6 often lead to charge transfer absorptions, a complicating feature if one wishes to discern transitions of the "dd" type in electronic spectra. Using ordinary and magnetically perturbed Mössbauer spectroscopy, the problem of distinguishing TP from TAP coordination is considered for a series of tris diimine compounds for which some of the structures are known crystallographically. The coordination environment is varied from near regular octahedral (twist angle $\phi = 60°$) toward trigonal prismatic ($\phi = 0°$) as shown in Figure 1. In this figure only one chelate ring structure is illustrated for each complex and the drawings for compounds **2**, **5**, **6**, and **7** are not meant to be suggestive of a particular choice of ϕ. The compounds investigated are part of a group of clathro-chelate systems recently discussed in the literature[1-3] and the details of nomenclature as well as structure may be found in ref 3. As the twist angle is decreased from 60° toward 0° in this series the quadrupole splitting (ΔE) increases from near zero to $\approx$ 1 mm/sec. The respective ΔE's including sign for some of the complexes and isomer shifts (in parentheses) relative to iron metal are also shown in Figure 1. Application of

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(1) J. E. Parks, B. E. Wagner, and R. H. Holm, *J. Amer. Chem. Soc.*, **92**, 3500 (1970).

(2) J. E. Parks, B. E. Wagner, and R. H. Holm, *Inorg. Chem.*, **10**, 2472 (1971).

(3) G. E. Larsen, G. N. La Mar, B. E. Wagner, J. E. Parks, and R. H. Holm, *Inorg. Chem.*, **11**, 2652 (1972).

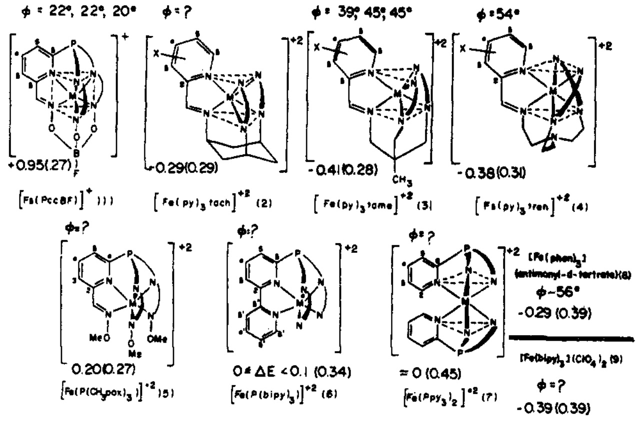

Figure 1.

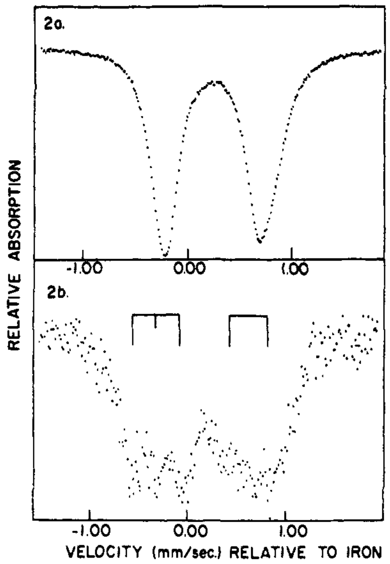

Figure 2.

transverse magnetic fields of the order 20 kG shows the sign of ΔE to be different for the extreme values of ϕ. For example the quadrupole splitting is *negative* for $Fe(phen)_3{}^{2+}$ ($\phi \sim 56$)[3] and $Fe(bipy)_3{}^{2+}$ (ϕ most probable greater than 50°) and *positive* (Figure 2) for the macrocyclic[3] encapsulation complex $Fe(PccBF)BF_4$ ($\phi = 22°$).[4,5]

In the limit of regular TAP coordination the central metal *valence* contribution to ΔE is zero for low-spin d^6, *i.e.*, the expectation values of the principal component (V_{zz}) of the electric field gradient tensor cancel for the filled t_{2g} manifold. The contribution from the fixed ligand charges is also *zero in the TP* as well as TAP limit. However, the valence contribution does not vanish in the TP limit as illustrated in Figure 3. It is reasonable to use the threefold axis as principal axis on twisting from TAP to TP. In this quantization the t_{2g} orbitals are[6] $t_{2g}{}^0 = d_{z^2}$, $t_{2g}{}^+ = \sqrt{2/3}d_{x^2-y^2} - \sqrt{1/3}d_{xz}$, and $t_{2g}{}^- = \sqrt{2/3}d_{xy} + \sqrt{1/3}d_{yz}$. Thus with twisting the coefficients of d_{xz} and d_{yz} vanish ($\phi \rightarrow 0°$)

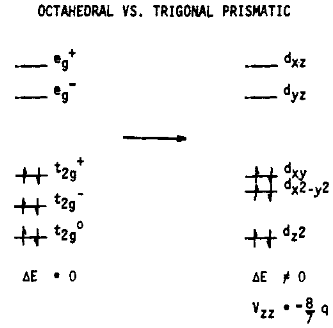

Figure 3.

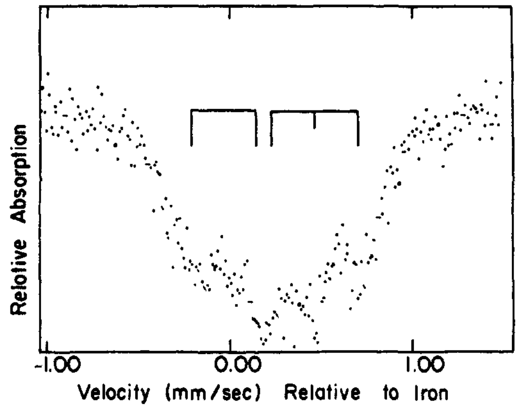

Figure 4.

and the crystal field ordering as well as nonzero valence contribution of the right of Figure 3 result. In addition this splitting must be *positive* for electron occupation.

The nonzero splittings observed in the TAP limit are usually small and due to covalence anisotropy. In the case of tris diimine systems this involves either elongation or compression along the threefold axis and the resulting differential covalent bonding to the orbitals of the t_{2g} set. The small *negative* ΔE's for $[Fe(phen)_3]^{2+}$, $[Fe(bipy)_3]^{2+}$, and $[Fe(py)_3tren]^{2+}$ (Figure 4) suggest such covalence anisotropy in the form of greater electron density in the $t_{2g}{}^0$ than $t_{2g}{}^{\pm}$. The zero ΔE of compound **7** is most consistent with a twist angle near 60° and near equivalent Fe–N bonds while the near-zero values for compounds **5** and **6** also suggest ϕ of the order 60°. On the other hand a system may be "twisted" toward the TP limit but have the positive quadrupole expected from the valence distribution reduced somewhat by a negative covalence contribution. Thus *small absolute values* of splitting alone cannot be taken as unambiguous evidence for large ϕ. The perturbed Mössbauer spectrum of compound **2** has been determined and although of relatively poor resolution, as in the case of compound **4** (Figure 4), V_{zz} is tentatively assigned as negative. This in conjunction with the small ΔE leads to the prediction that this system is probably near the TAP limit.

In conclusion a large *positive* quadrupole is expected in the TP limit in the absence of significant covalence anisotropy. Furthermore, the composition of the three lowest single electron d orbitals for a trigonal prism (Figure 3) is clearly verified by the perturbed Mössbauer spectrum.

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(4) M. R. Churchill and A. H. Reis, Jr., *Chem. Commun.*, 1307 (1971).

(5) M. R. Churchill and A. H. Reis, Jr., *Inorg. Chem.*, **11**, 2299 (1972).

(6) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill, New York, N. Y., 1962, p 68.

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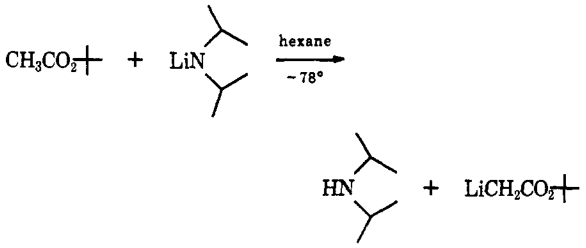
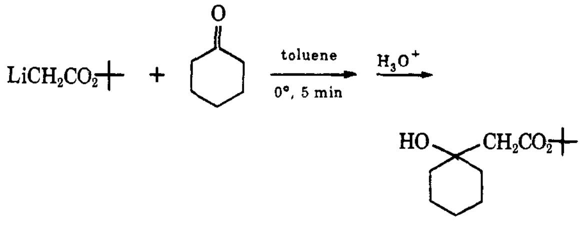
Isolation and Characterization of Lithio *tert*-Butyl Acetate, a Stable Ester Enolate

Sir:

Addition of *tert*-butyl acetate to lithium diisopropylamide in hexane furnishes lithio *tert*-butyl acetate as a stable white solid. This ability to isolate a solid ester enolate provides an exceedingly simple method for conducting Reformatsky-type reactions. For example, the following conversions (eq 2 and 3) were obtained in less than 15 min using stoichiometric amounts of lithio *tert*-butyl acetate weighed in air.

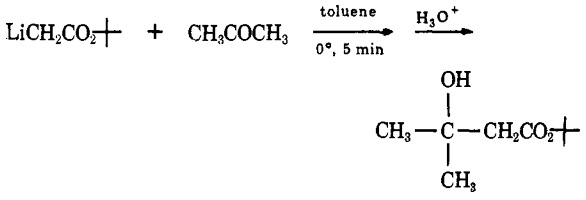


(1)



(2)

100% (glpc)



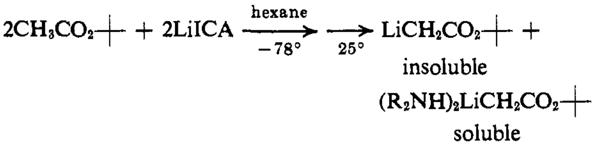
(3)

100% (glpc)

Tetrahydrofuran solutions of a variety of lithium ester enolates may be obtained by reaction of the appropriate ester with lithium *N*-isopropylcyclohexylamide (LiICA).[1] However, attempts to remove the solvent and amine from these solutions even at −78° only yield oily yellow residues containing mostly condensed ester.

LiICA is highly soluble in hydrocarbon solvents, forming 1 *M* solutions in hexane at −78°. It seemed likely that the lower molecular weight ester enolates would be insoluble in such solvents and, accordingly, we attempted to prepare lithio ethyl acetate in hexane. Addition of ethyl acetate to a solution of LiICA in hexane at −78° produces a white precipitate. However, attempts to isolate this material by filtration, even at −78°, result in extensive condensation to form the lithium salt of ethyl acetoacetate.

Addition of *tert*-butyl acetate to hexane solutions of LiICA gives entirely different results. At −78°, the solution remains colorless and no precipitate is formed. When the solution is allowed to reach 25°, a white solid gradually settles out. Filtration produces lithio *tert*-butyl acetate in 50% yield. Recooling to −78° prior to filtration does not increase the yield. Subsequently, we discovered that lithio *tert*-butyl acetate is only slightly soluble in hexane (<0.1 g/100 ml), but is dissolved by hexane solutions containing *N*-isopropylcyclohexylamine. The solubility at 25° is such that 2 mol of the amine dissolves 1 mol of the enolate. Similar results were obtained with other secondary amines, including diisopropylamine and hexamethyldisilazane. Consequently, the 50% yield of enolate is readily explained by the following reaction (eq 4).



(4)

The isolated yield can be made nearly quantitative by choosing the more volatile diisopropylamine, which can be removed by vacuum distillation. Although lithium diisopropylamide is only slightly soluble in hexane at −78°, addition of *tert*-butyl acetate results in immediate dissolution. Evaporation of the solvent and amine at room temperature and reduced pressure produces lithio *tert*-butyl acetate as a white powder in yields of 95–100%.

Solid lithio *tert*-butyl acetate is remarkably stable. Heated under a nitrogen atmosphere, it decomposes only at temperatures higher than 110°. Samples of the enolate have been stored in sealed bottles on the shelf for several months with no change in purity. The solid may be exposed to air for brief periods without extensive hydrolysis. Prolonged exposure results in a gradual decrease in weight, presumably through formation and evaporation of *tert*-butyl acetate, but the solid remains colorless with no evidence of condensation.

Lithio *tert*-butyl acetate forms 1 *M* solutions in benzene or toluene at 25°. These solutions are not stable, but with carefully dried solvents, condensation is less than 5% after 3 hr. The proton nmr spectrum of the benzene solution provides the first clear evidence of an oxygen–lithium bonded structure for an ester enolate I.[2] Two partially resolved doublets are observed at 3.14 and 3.44 ppm (downfield from internal TMS) for the two α hydrogens in the anion. The singlet of the *tert*-butyl grouping appears at 1.56

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(1) M. W. Rathke and A. Lindert, *J. Amer. Chem. Soc.*, **93**, 2318 (1971).

(2) Using ir spectral evidence, Vaughn[3] assigned a zinc–oxygen bonded structure to the Reformatsky reagent obtained from zinc and ethyl bromoisobutyrate in ether–benzene solution. Gaudemar[4] has assigned a range of structures for the reagent obtained from zinc and ethyl bromoacetate in more polar solvents such as tetrahydrofuran or dimethyl sulfoxide.

(3) W. R. Vaughn, S. C. Bernstein, and M. E. Larber, *J. Org. Chem.*, **30**, 1790 (1965).

(4) M. Gaudemar and M. Martin, *C. R. Acad. Sci. Paris, Ser. C*, **267**, 1053 (1968).