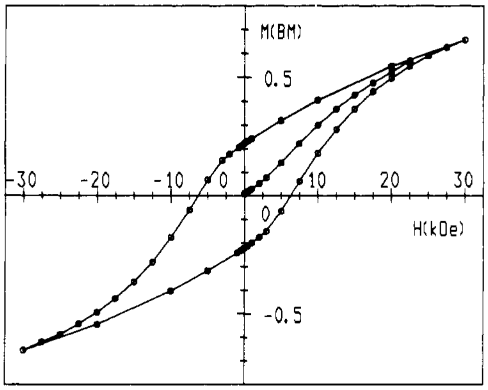

Figure 4. Field dependence of the magnetization of a powdered sample of **1** at 4.2 K.

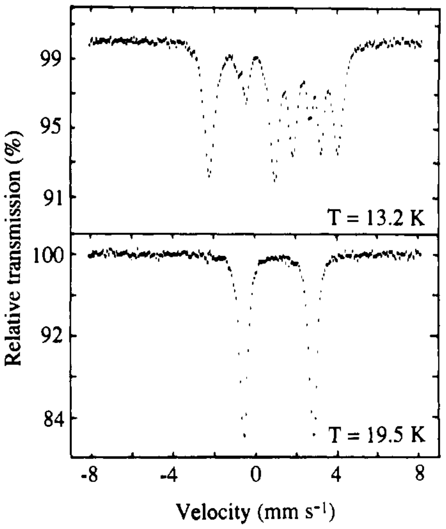

Figure 5. Mössbauer spectra of **1** at 19.5 and 13.2 K.

A close examination of the X-ray molecular structure allows us to explain the origin of the weak ferromagnetism observed. The electronic structure of the iron(II) ion results from competing effects between spin coupling and local distortion. Due to the angle between the O(2)″–Fe–O(2)‴ directions of adjacent molecules in a sheet (94.65 (4)°), the relative orientations of adjacent ferrous coordination polyhedra result in the presence of two spin sublattices. The competition between this local effect and the antiferromagnetic exchange interaction mediated by the acetato bridges between adjacent ferrous ions affords a magnetic ground state within each layer. Finally, it can be assumed that the interactions between these magnetic layers through the hydrogen-bonding network described in Figure 2 promote the three-dimensional ferromagnetic ordering observed.

Work in progress includes high-field magnetization measurements, a frequency-dependent ac magnetic susceptibility study, and specific heat and neutron diffraction powder diagram studies.

Acknowledgment. The CNRS and the National Hellenic Research Foundation are acknowledged for partial support of this work. M.-A.M.-L. thanks the Commission of European Communities (Science Program) for a doctoral fellowship.

Supplementary Material Available: An ORTEP view of the complex molecule of **1** displaying numbering of the atoms and tables of crystallographic data, atomic positional and thermal parameters, bond distances and angles, components of the anisotropic temperature factors, and deviations of atoms from their least-squares planes (8 pages); a listing of observed and calculated structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

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(14) Cromer, D. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1, p 149.

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Dicarbollide Complexes of Thallium: Structural and ^{11}B NMR Studies

Recently there has been a great deal of interest in organometallic compounds involving the heavier Group 13 elements, with particular relevance to the bonding in monovalent complexes of thallium and indium.[1] Dicarbollide complexes incorporating thallium(I) were first prepared by Stone[2] and have been used extensively as synthons in metallacarborane chemistry.[3] In order to further explore the structural chemistry of thallium dicarbollide complexes, the anionic thallacarborane [*closo*-3,1,2-$TlC_2B_9H_{11}$]$^-$ (**1**) was prepared as the (PPN)[4] salt by anhydrous metathesis of (Tl)**1**[2] with [PPN]$^+$Cl$^-$ in CH_3CN. This monothallacarborane complex, [PPN]**1**, is very soluble in coordinating solvents such as THF[4] or CH_3CN, in marked contrast to the dithallium precursor. The solid-state structure of [PPN]**1** was established by a single-crystal X-ray diffraction study,[5] which showed well-

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(1) (a) Janiak, C.; Hoffmann, R. *J. Am. Chem. Soc.* **1990**, *112*, 5924. (b) Janiak, C.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1688. (c) Beachley, O. T., Jr.; Churchill, M. R.; Fettinger, J. C.; Pazik, J. C.; Victoriano, L. *J. Am. Chem. Soc.* **1986**, *108*, 4666 and references contained therein.

(2) Spencer, J. L.; Green, M.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1972**, 1178.

(3) See, for example: (a) Manning, M. J.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1988**, *110*, 4458. (b) Do, Y.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1987**, *109*, 1853.

(4) (PPN)$^+$Cl$^-$ = bis(triphenylphosphoranylidene)ammonium chloride. THF = tetrahydrofuran.

(5) (PPN)**1**: (a) Pale yellow parallelepiped single crystals from a $CH_3CN/(C_2H_5)_2O$ solution. (b) $a = 15.006$ (2) Å, $b = 18.964$ (2) Å, $c = 16.178$ (2) Å, $\beta = 112.231$ (3)°, $V = 4258$ Å^3, $Z = 2$ (two dimeric anions and four cations per unit cell), space group $P2_1/n$, 3509 independent reflections with $I > 3\sigma(I)$, R (R_w) = 0.067 (0.077). (c) Diffraction data were collected at 298 K in the θ–2θ scan mode for 7519 unique reflections having $2\theta < 50°$ on a diffractometer constructed by Prof. C. E. Strouse of UCLA using graphite-monochromated Mo Kα radiation. (d) Data were corrected for Lorentz, polarization, and absorption effects. Atoms were located by use of the heavy-atom method, and SHELX76 was used for structure factor calculations and full-matrix least-squares refinement.

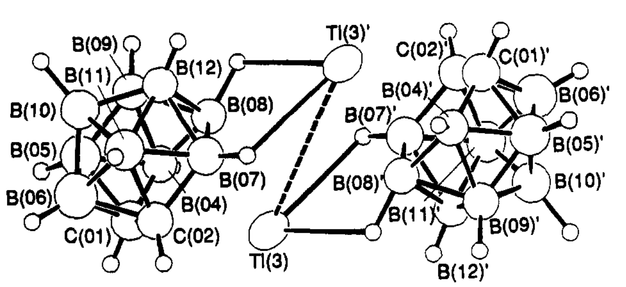

Figure 1. Structure of $[closo\text{-}3,1,2\text{-}TlC_2B_9H_{11}]^-$ (**1**) showing the atom-labeling scheme. Selected distances (Å) from Tl: to B(8), 2.664 (7); to B(4), 2.744 (8); to B(7), 2.741 (7); to C(1), 2.915 (6); to C(2), 2.923 (6). Because this anion is centrosymmetric, only the labeling of the left-hand ligand conforms to convention. Hydrogen atoms have been drawn with artificially small temperature factors.

separated PPN cations and discrete, "dimeric" anions. The anion of [PPN]**1** is displayed in Figure 1. There is a center of symmetry between the two thallium atoms with an internuclear separation between the two Tl centers of 4.241 (1) Å.[6] A solid-state structure determination had previously been reported for the $[Ph_3PMe]^+$ salt of **1**;[7] rather surprisingly, the closest Tl–Tl distance was found to be 7.967 Å, almost twice that for the aforementioned $[PPN]^+$ complex. The different intermolecular arrangement found in the two salts of **1** certainly supports a role for the cation in the closer Tl–Tl distances in the solid-state structure of [PPN]**1**.

The possible existence of a homonuclear bonding interaction between two Tl(I) centers has been described for the "dimer" $\{Tl[C_5(CH_2C_6H_5)_5]\}_2$ (**2**) wherein the Tl–Tl separation in the solid state was found to be 3.63 Å.[1,8] In this case the significance of the L–Tl–Tl (L = ligand ring centroid) angle was demonstrated; the trans-bent geometry leads to a more favorable Tl–Tl bonding interaction. The comparable angle found in **2** is 131.8°; this is quite different from the rather acute L′–Tl–Tl (L′ = basal boron B(10)) angle of 76.2° for the dimeric thallacarborane [PPN]**1**.[10] For the thallacarborane, the dicarbollide ligand is bonded in a pentahapto fashion with *one* of the thallium centers while at the same time this ligand is approximately in a "bridging" position between the *two* thallium ions. This bridged array is stabilized by a set of metal–hydrogen–boron (M–H–B) interactions between the terminal hydrogens of one dicarbollide ligand and the thallium which is "capping" the other dicarbollide ligand; this is illustrated in Figure 1. Numerous examples of M–H–B interactions have been cited throughout metallaborane and metallacarborane chemistry,[11] and while the distances found here are rather long (Tl(3)′–H(08) = 2.62(11) Å and Tl(3)–H(07) = 2.83(11) Å for **1**), they compare rather well with previously reported metal–hydrogen separations when one considers the relative size of the thallium (I) ion.[12] A recent report describes a *closo*-indacarborane dimer in which the monomeric In(III) units appear to be stabilized in a similar fashion by M–H–B interactions.[13]

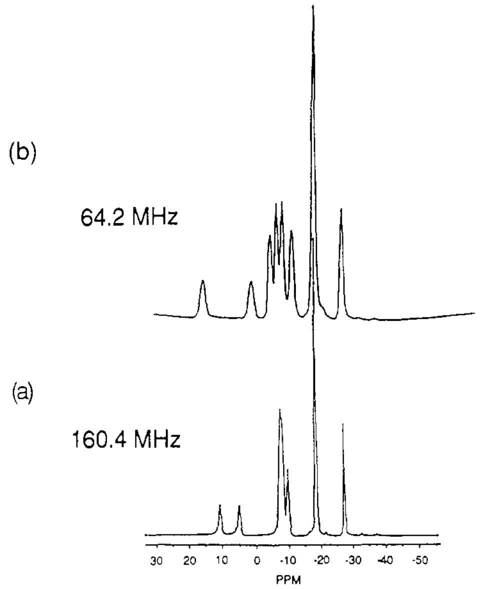

Figure 2. (a) 160.4-MHz and (b) 64.2-MHz $^{11}B\{^1H\}$ NMR spectra of $[PPN][closo\text{-}3,1,2\text{-}TlC_2B_9H_{11}]$ ([PPN]**1**) in CH_3CN at 25 °C. $^{11}B\{^1H\}$ NMR (ppm, CH_3CN): (160.4 MHz) δ 10.5, 4.8, −6.9, −9.9, −18.7, −27.6; (64.2 MHz) δ 15.1, 1.0, −4.7, −6.8, −8.6, −11.6, −18.6, −27.4.

While the structure determination indicates a dimeric relationship in the solid state between pairs of monothallacarborane anion moieties, ^{11}B NMR spectra actually support the existence of a strong *intra*molecular interaction between the thallium ion and the dicarbollide ligand in solution. The 160.4 MHz $^{11}B\{^1H\}$ NMR spectrum of [PPN]**1** (in CH_3CN) displayed in Figure 2a consists of six distinct resonances that do not unambiguously integrate for the nine borons of the dicarbollide ligand; going from low field to high field, the relative integrated intensities are $^1/_2$:$^1/_2$:3:1:3:1. The possibility of a 50:50 mixture of two isomers was discounted by obtaining the spectrum at a different field strength. The $^{11}B\{^1H\}$ NMR spectrum of PPN**1** obtained at 64.2 MHz, shown in Figure 2b, when compared with the high-field spectrum is supportive of a coupling interaction between some of the boron nuclei and a spin $^1/_2$ nucleus other than ^1H. Taken together, the spectra show that with the exception of the two most upfield resonances at −27.6 and −18.7 ppm (integrated intensities of 1 and 3, respectively), all other (downfield) signals are attributable to boron nuclei that are coupled to a spin $^1/_2$ nucleus. Thallium has two spin $^1/_2$ nuclei, ^{205}Tl (70.5% natural abundance) and ^{203}Tl (29.5% natural abundance), with ^{205}Tl being the third most receptive spin $^1/_2$ nucleus known following ^1H and ^{19}F.[14] The coupling pattern consists of three sets of doublets having coupling constants of 910, 480, and 100 Hz. From the results of a two-dimensional COSY ^{11}B–^{11}B proton decoupled NMR spectrum, these were assigned, respectively, to the unique upper belt boron B(8), symmetrical upper belt borons B(4) and B(7), and to the two borons (B(9) and B(12)) on the lower belt directly beneath the unique boron.[15] A similar coupling pattern was also seen in

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(6) A single-crystal X-ray structure determination has been carried out on the *C*-substituted dimethyl derivative of [PPN]**1**, $[PPN][closo\text{-}1,2\text{-}(CH_3)\text{-}3,1,2\text{-}TlC_2B_9H_9]$. The interatomic distance between the two thallium ions is 4.091 (1) Å. The bonding geometry is nearly identical with that of the unsubstituted derivative. Details of the structure determination will be forthcoming in a full paper.

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(8) A recent report has appeared describing the structure determination of $[Tl][closo\text{-}1,2\text{-}(CH_3)_2\text{-}3,1,2\text{-}TlC_2B_9H_9]$: Jutzi, P.; Wegener, D.; Hursthouse, M. B. *Chem. Ber.* **1991**, *124*, 295.

(9) Schumann, H.; Janiak, C.; Pickardt, J.; Borner, U. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 789.

(10) The angle formed by B(10)–Tl(3)–Tl(3′) closely approximates the upper belt ring centroid–Tl–Tl angle.

(11) Grimes, R. N. In *Metal Interactions with Boron Clusters*; Grimes, R. N., Ed.; Plenum Press: New York, 1982; Chapter 7 and references contained therein.

(12) The covalent radius of Tl(I) has been estimated as 1.48 Å; see ref 7a and the references contained herein. The ionic radius for the thallous ion has been estimated to be between 1.5 and 1.7 Å (depending on coordination number): Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *A32*, 751.

(13) Hosmane, N. S.; Lu, K. J.; Zhang, H.; Cowley, A. H.; Mardones, M. A. *Organometallics* **1991**, *10*, 392. The authors do not discuss the probable existence of an M–H–B interaction in the solid state or the effect of this interaction on the short internuclear In–In separation although the reported distances support such an interaction.

(14) Hinton, J. F.; Metz, K. R.; Briggs, R. W. *Prog. NMR Spectrosc.* **1988**, *20*, 423 and the references contained therein.

the ^{11}B NMR spectra of the C-substituted (both dimethyl and monomethyl) derivatives of [PPN]**1**.[16]

The observation that $^2J(^{205}\mathrm{Tl}-^{11}\mathrm{B})$ couplings are much smaller than $^1J(^{205}\mathrm{Tl}-^{11}\mathrm{B})$ couplings is consistent with the ^{11}B NMR spectrum of $[\mathrm{TlMe_2}]^+[\mathrm{Me_2TlB_{10}H_{10}}]^-$ (**3**).[17] This Tl(III) metallaborane complex exhibits a maximum $^1J(^{205}\mathrm{Tl}-^{11}\mathrm{B})$ of 258 Hz, which is attributed to the boron nuclei directly bound to the thallium. The large $^1J(^{205}\mathrm{Tl}-^{11}\mathrm{B})$ values seen in the spectrum of **1** are, to the best of our knowledge, the largest ^{205}Tl coupling constants yet observed for a Tl(I) complex.[18] Due to the highly ionic nature of these complexes, there have been only a few spin–spin coupling constants reported.[13] This strong coupling interaction is most likely a direct consequence of the sp^n-hybridized bonding orbitals of the dicarbollide ligand. The directional nature and substantial s character possessed by these orbitals would be expected to lead to larger coupling relative to complexes with pure p character in their bonding orbitals (i.e. ligands such as $C_5H_5^-$ and $C_5Me_5^-$).

Calculations concerning the bonding interactions in these thallium dicarbollide complexes have been carried out, and these results together with additional structural and spectroscopic details will be forthcoming in a full paper.

Acknowledgment. This work was supported in part by the Office of Naval Research (UCLA) and the Korea Science and Engineering Foundation (KAIST). We would also like to thank Dr. A. Varadarajan for helpful discussions and Andrea Oyeung for the illustrations.

Supplementary Material Available: Contour plot of a COSY-90 experiment, details of the synthesis of [PPN]**1**, and tables of crystallographic data collection, atom coordinates and anisotropic thermal parameters, bond distances and angles, and hydrogen atom positions and thermal parameters (8 pages); a table of observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

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(15) A two-dimensional COSY ^{11}B–^{11}B proton-decoupled NMR spectrum of **1** (see supplementary material) supports these assignments through the connectivity pattern established in the contour plot. A single boron gives rise to the doublet with 900-Hz coupling. This boron is directly linked to the 480-Hz doublet. The low-frequency component of the 900-Hz doublet shows off-diagonal correlation with the low-frequency component of the 480-Hz doublet. The same situation exists between the high-frequency components of the two doublets. There are no interdoublet off-diagonal correlations between the low-frequency and the high-frequency components. This same relationship was observed in the 2-D ^{11}B NMR spectrum of $[\mathrm{Me_2TlB_{10}H_{12}}]^-$ ($\mathbf{3}^-$).[17] These authors suggested that the absence of any high-frequency/low-frequency component correlation indicates that the relative signs of the observed ^nJ-(^{205}Tl–^{11}B) are all the same, presumably positive.

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(17) Beckett, M. A.; Kennedy, J. D.; Howarth, O. W. *J. Chem. Soc., Chem. Commun.* **1985**, 855.

(18) The spin–spin coupling exists irrespective of the choice of solvents (both coordinating and noncoordinating solvents). The choice of cation is not important, and the sparingly soluble parent dithallium complex $\mathrm{Tl^+}$-$[\mathrm{TlC_2B_9H_{11}}]^-$ also exhibits the coupling in THF. No evidence for coupling to ^{205}Tl was seen in the ^{1}H NMR spectrum. Attempts to obtain a ^{205}Tl NMR spectrum were unsuccessful, most likely due to coupling of Tl with the quadrupolar boron nucleus.

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Reversible Coordination of Diphenylacetylene to the Dicarbidodecaruthenium Framework. Substitution-Induced Metal–Metal Bond Formation

Much of what is known about high-nuclearity transition-metal carbonyl clusters naturally concerns their preparation and structural characterization;[1,2] only in cases involving especially robust metal frameworks, recent examples being "$\mathrm{Ru_6C}$"[3] and "$\mathrm{Re_7IrC}$",[4] has systematic derivative chemistry with organic reagents been explored. Prompted in part by a recent report of the degradation of $[\mathrm{Ru_{10}C(CO)_{24}}]^{2-}$[5] under mild exposure to carbon monoxide,[6] we wish to present contrasting results with $[\mathrm{Ru_{10}C_2(CO)_{24}}]^{2-}$[7] that demonstrate structural integrity for the "$\mathrm{Ru_{10}C_2}$" framework under (reversible) substitution by diphenylacetylene.

The reactions of alkynes with high-nuclearity clusters have generally displayed the same features as for smaller clusters, namely, coordination of alkynes as intact molecules to multiple metal centers as well as products resulting from the activation of C≡C or C—H bonds.[1,2,8] Two major types of alkyne ligand–cluster interaction have thus far been recognized, i.e., the insertion of alkynes into metal–metal bonds, resulting in extensive metal framework rearrangement, or μ_3-η^2-coordination of an alkyne to a triangular face of the original metal polyhedron. The reaction of diphenylacetylene with $[\mathrm{Ru_{10}C_2(CO)_{24}}]^{2-}$ (see Scheme I) illustrates a third possible consequence of an alkyne–cluster interaction, namely, coordination-induced metal–metal bond formation. Furthermore, this chemical and structural change is reversed by added carbon monoxide.

$[\mathrm{Et_4N}]_2[\mathrm{Ru_{10}C_2(CO)_{24}}]$ and diphenylacetylene (ca. 6 equiv) were heated in dry diglyme at 125 °C for 5 days until the growth of a new set of IR (ν_{CO}) bands was complete. After removal of the solvent, the dark purple residue was placed on a deactivated (5% H_2O) neutral alumina column. Elution with dichloromethane provided a major purple band, which was collected and crystallized from dichloromethane–diethyl ether at −25 °C to give thin needles (70% yield). Formulation of the product as $[\mathrm{Et_4N}]_2[\mathrm{Ru_{10}C_2(CO)_{22}(C_2Ph_2)}]$ was based on analytical and spectroscopic data.[9] In the reverse reaction, $[\mathrm{Ph_3PCH_2CH_2PPh_3}][\mathrm{Ru_{10}C_2(CO)_{22}(C_2Ph_2)}]$[10a] in diglyme was heated at 125 °C under a carbon

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(9) Anal. Calcd for $\mathrm{C_{54}H_{50}N_2O_{22}Ru_{10}}$ ($[\mathrm{Et_4N}]_2$**2**): C, 31.03; H, 2.41; N, 1.34. Found: C, 31.32; H, 2.44; N, 1.30. IR (dichloromethane): ν_{CO} 2042 (w), 2006 (s), 1999 (vs), 1980 (w, sh), 1927 (w, br), 1812 (w), 1786 (w) cm^{-1}. ^{1}H NMR (acetone-d_6, 20 °C): δ 7.26 (m, 10 H, C_6H_5), 3.47 (q, 16 H, $J_{\mathrm{H-H}} = 7.3$ Hz, $\mathrm{CH_3C}H_2$–), 1.37 (tt, 24 H, $J_{\mathrm{H-H}} = 7.3$ Hz, $J_{\mathrm{N-H}} = 1.9$ Hz, $\mathrm{C}H_3\mathrm{CH_2}$–). FAB-MS (negative ion, ^{102}Ru): m/z 1968 (M − $\mathrm{Et_4N}$).

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