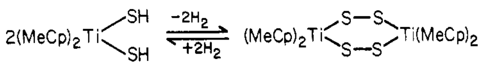

(4)

Acknowledgment. This research was supported by the National Science Foundation and the Research Corp. Field desorption mass spectrometry facilities are supported by the National Cancer Institute. High-field NMR facilities were provided by the National Science Foundation (NSF Grant CHE 79-16100).

Registry No. 1a, 12300-91-3; **1b**, 78614-86-5; **2a**, 12307-22-1; **2b**, 78614-88-7; **3**, 15390-38-2; **4b**, 79816-62-9; [Ir(dppe)$_2$S$_2$]Cl, 40603-50-7; [Ir(dppe)$_2$Se$_2$]Cl, 40603-51-8; (MeCp)$_2$Ti(SH)$_2$, 79816-63-0; P(n-Bu)$_3$, 998-40-3.

Racemization of Chiral Tetrahedral Organotransition-Metal Clusters: A Novel Fluxional Process

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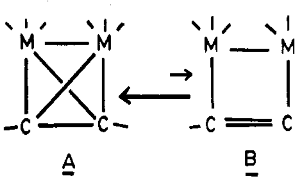
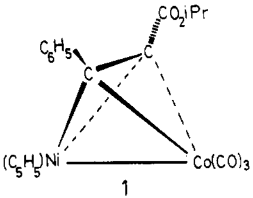
Summary: The intrinsically chiral tetrahedral organotransition-metal clusters PhC≡CCO$_2$CHMe$_2$[(C$_5$H$_5$)Ni—M], where M is Co(CO)$_3$ (**1**), (C$_5$H$_5$)Mo(CO)$_2$ (**2**), or Mn(CO)$_4$ (**3**), have been prepared. The low symmetry of these molecules allows the detection and analysis of a new fluxional process, viz., the formal rotation of the M—M and C—C bond vectors. Using high-field NMR spectroscopy, $\Delta G^{\ddagger}$ for **2** is 20.5 ± 0.5 kcal/mol. The fluxionality and high reactivity of these molecules toward addition of an Fe(CO)$_3$ moiety are rationalized in terms of Wade's rules for electron-deficient clusters.

While many of the recent advances in cluster chemistry[1] have focussed on larger and larger molecular assemblies, the oldest and most widely investigated systems[2] still pose fascinating challenges not only of synthesis but also of bonding and molecular dynamics. Thus, to rationalize the high reactivity of the acetylene clusters A such as μ-(η^2-R$_2$C$_2$)Co$_2$(CO)$_6$, it was suggested more than a decade ago[3] that they might be in equilibrium with the isomeric 1,2-dimetallacyclobutenes B (Scheme I). Although some extremely interesting observations have been reported,[4] there has been, to our knowledge, no unequivocal demonstration of a process corresponding formally to relative rotation of the C–C and M–M bond vectors in a tetrahedral cluster. Furthermore, calculations suggest that, for such an interconversion process to occur, a relatively high barrier must be surmounted.[5] We now report the construction of molecules possessing appropriate functionalities to allow us to probe the viability of such a process.

Scheme I



We have found that the reaction of Co$_2$(CO)$_8$, (C$_5$H$_5$)$_2$Ni and an alkyne yields (inter alia) molecules of the type (C$_5$H$_5$)NiCo(CO)$_3$(RC≡CR).[6] Similarly, the new mixed dimetallic series (C$_5$H$_5$)NiMo(CO)$_2$(C$_5$H$_5$)(RC≡CR) is readily accessible by treatment of an alkyne with (C$_5$H$_5$)$_2$Ni and (C$_5$H$_5$)$_2$Mo$_2$(CO)$_6$.[8,9] When the precursor acetylene bears two different substituents, these molecules are chiral and the incorporation of an isopropyl moiety, as in (C$_5$H$_5$)NiCo(CO)$_3$(PhC≡C—CO$_2$CHMe$_2$) (1) and (C$_5$H$_5$)NiMo(CO)$_2$(C$_5$H$_5$)(PhC≡C—CO$_2$CHMe$_2$) (2) provides diastereotopic methyl groups with which to monitor the rate of racemization of the complex and thus unmask the hitherto hidden process. In the absence of exchange the isopropyl methyls exhibit a pair of doublets which only



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(1) For a recent review, see: "Transition Metal Clusters"; Johnson, B. F. G., Ed.; Wiley-Interscience: New York, 1980.

(2) See, for example: Pino, P.; Braca, G. In "Organic Syntheses via Metal Carbonyls"; Wender, I., Pino, P., Eds.; Wiley-Interscience: New York, 1977; Vol. 2, p 419.

(3) Iwashita, Y.; Tamura, F.; Wakmatsu, H. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 1520–1523.

(4) (a) Dickson, R. S.; Pain, G. N. *J. Chem. Soc., Chem. Commun.* **1979**, 277–278. (b) Boag, N. M.; Green, M.; Stone, F. G. A. *Ibid.* **1980**, 1281–1282.

(5) Calculations on Cp$_2$Ni$_2$(C$_2$H$_2$) yield a barrier of 20.7 kcal/mol; Hoffmann, R.; Hoffman, D., personal communication.

(6) Co$_2$(CO)$_8$ (1 g, 2.9 mmol), (C$_5$H$_5$)$_2$Ni (1 g, 5.3 mmol), and C$_6$H$_5$C$_2$CO$_2$CHMe$_2$ (1 g, 5.3 mmol) were heated at 100 °C in heptane under N$_2$ for 6 h and gave rise to the heterobimetallic acetylene complex 1 [25% yield; oil, m/z 453.9756, calcd m/z 453.9761; ^{1}H NMR (80 MHz) δ 7.66, 7.35 (m, C$_6$H$_5$), 5.31 (s, C$_5$H$_5$), 1.29 (d, CH$_3$, J = 6.6 Hz) in CD$_2$Cl$_2$ at 22 °C; δ (in C$_6$D$_6$ at 22 °C) 1.13 (d, CH$_3$, J = 6.4 Hz); IR (neat liquid) ν_{CO} 2055 (s), 2000 (vs), 1700 (s) cm^{-1}] as the main product together with (inter alia) Ni$_2$Cp$_2$(CO)$_2$, Co$_2$(CO)$_6$(PhC$_2$CO$_2$-i-Pr), Ni$_2$Cp$_2$(PhC$_2$CO$_2$-i-Pr), and Co$_2$(CO)$_4$(PhC$_2$CO$_2$-i-Pr)$_3$. These products were easily separated by TLC on silica gel using petroleum ether/ether (9:1). An alternative but less direct mode of access to the mixed bimetallic complex (μ-C$_6$H$_5$C$_2$C$_6$H$_5$)[(CO)$_3$Co–Ni(η^5-C$_5$H$_5$)] has recently appeared involving the reaction of (C$_5$H$_5$)$_2$Ni$_2$(PhC$_2$Ph) with Co$_2$(CO)$_8$ (24% yield). The X-ray structural determination shows the acetylene bonded perpendicularly to the metal–metal bond.[7]

(7) Freeland, B. H.; Hux, J. E.; Payne, N. C.; Tyers, K. G. *Inorg. Chem.* **1980**, *19*, 693–696.

(8) (C$_5$H$_5$)$_2$Ni (1 g, 5.3 mmol), (C$_5$H$_5$)$_2$Mo$_2$(CO)$_6$ (1.3 g, 2.7 mmol), and PhC$_2$CO$_2$-i-Pr (1 mL, 5.3 mmol) were heated at 105 °C in 35 mL toluene for 7 h under N$_2$. TLC as before afforded 1.19 g (40%) of **2** as a red-brown crystalline solid: mp 90–91 °C; m/z 529.9922, calcd 529.99254; IR (heptane) ν_{CO} 2030 (w), 1978 (sh), 1968 (vs), 1930 (s), 1902 (m), 1857 (s), 1682 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$ at 30 °C at 80 MHz) δ 7.54, 7.25 (m, Ph), 5.24 (s, Cp), 5.14 (s, Cp), 1.35 (d, CH$_3$, J = 6.4 Hz); (in C$_6$D$_6$ at 30 °C) δ 1.22, 1.17 (dd, CH$_3$, J = 6.1 Hz)] together with Ni$_2$Cp$_2$(CO)$_2$, Ni$_2$Cp$_2$(PhC$_2$CO$_2$-i-Pr), and unreacted Mo$_2$Cp$_2$(CO)$_6$. Similarly, other heterobimetallic species are accessible (e.g., (μ-PhC$_2$CO$_2$-i-Pr)[(CO)$_4$MnNi(η^5-C$_5$H$_5$) (**3**), mp 128 °C, was obtained from Mn$_2$(CO)$_{10}$ and Cp$_2$Ni in 40% yield).

(9) The 1857-cm^{-1} band in **2** suggests the presence of a semibridging carbonyl as in [CpMo(CO)$_2$]$_2$C$_2$R$_2$: Bailey, W. I.; Chisholm, M. H.; Cotton, F. A.; Rankel, L. A. *J. Am. Chem. Soc.* **1978**, *100*, 5764.

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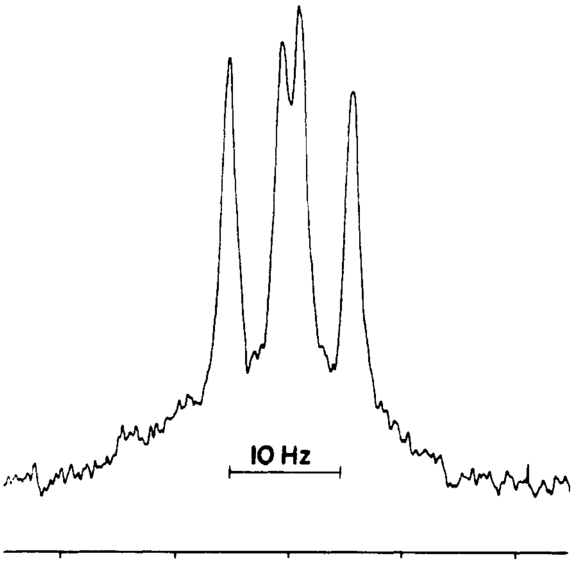
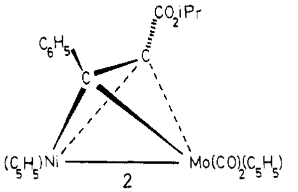


Figure 1. Proton NMR spectrum (400 MHz) of **1** at 20 °C in C_6D_6 (methyl region).



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coalesce to one doublet when the rate of racemization is fast on the ^{1}H NMR time scale.[10] For the complex **1**, this situation obtains over the temperature range 298–383 K. As shown in Figure 1, the two doublets expected for the methyls in a chiral environment are apparent at 20 °C in C_6D_6 by using a 9.395 T field (400 MHz) (δ 1.094, 1.082 ($\Delta\delta$ = 0.012 ppm, $^3J_{HH}$ = 6.25 Hz)). In toluene, at this temperature, the spectrum exhibits only three peaks owing to the overlapping of the two central signals. In this solvent, the coalescence temperature was reached at ~378 K and $\Delta G^\ddagger$ = 20.5 ± 0.5 kcal/mol. For the complex **2**, the low temperature limiting spectrum (two doublets) (see Figure 2) persists up to ~340 K in C_6D_6 and true coalescence has not quite occurred in toluene-d_8 even at 383 K.[11] To account for the facile racemization of these molecules, one must invoke a mechanism which corresponds formally to relative rotation of the C—C and M—M bond vectors. An obvious possibility is dissociation of the alkyne ligand followed by reassociation to give the other enantiomer. However, exchange between free and complexed alkynes was not observed under the conditions of the NMR experiment. Of the intramolecular possibilities the tetrahedral–square-planar interconversion (as originally proposed for (RC≡CR) $Co_2(CO)_6$[3]) must be considered; there exists also the attractive idea of metal–metal bond cleavage to give a butterfly cluster which could then invert, reform the metal–metal bond, and give the other enantiomer.

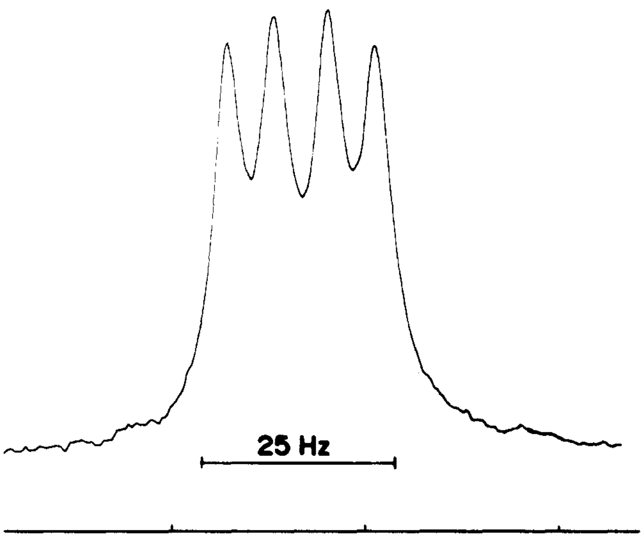
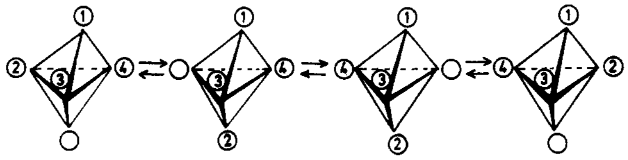


Figure 2. Proton NMR spectrum (250 MHz) of **2** at 30 °C in C_6D_6 (methyl region).

Scheme II



Fluxionality in these nominally saturated systems[12] is perhaps somewhat surprising and, rather than regarding these metal atoms as being in 18-electron environments, we take as a starting point Wade's model[13] in which these tetrahedral clusters possess six skeletal electron pairs and are formally classifiable as nido trigonal bipyramids. One can readily visualize, for example, the intermediacy of the alternative trigonal-bipyramidal geometry with the vacancy in the equatorial plane as in Scheme II. This leads to a butterfly-type intermediate *without* scission of a formal two-electron bond; indeed, the ready fluxionality of these molecules is merely symptomatic of a low barrier to rearrangement because of the vacancy on the cluster surface. Taking the viewpoint of these molecules as nido clusters with a vacant coordination position, it is easy to account for their reactivity, particularly the extreme ease of addition of the $Fe(CO)_3$ moiety[14] to these supposedly saturated clusters without the need for thermal or photochemical initiation. One might be tempted to regard the $Fe(CO)_3$ adduct (which is square pyramidal[14] with an iron atom capping the basal plane comprised of the four original cluster moieties) as arising from $Fe(CO)_3$ trapping of the nido trigonal bipyramid with the cluster vacancy in the equatorial position.

A number of tetrahedral clusters which are chiral by virtue of the asymmetry of the arrangement of ligands[15] (rather than having an inherently chiral cluster of four different skeletal atoms) have been studied by NMR

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[10] One must sound a cautionary note that the mere observation of a doublet is insufficient evidence on which to presume rapid interconversion since small chemical shift differences between the diastereotopic methyls are the norm in the systems we have studied. The data reported here for compound 1 were obtained at 400 MHz. This complex shows only a doublet in any solvent at 80 MHz (see ref 6).

[11] A Catch-22 exists here in that a high-field instrument is required to provide chemical shift discrimination between the methyls, yet use of such high fields raises the coalescence temperature near to the decomposition temperature of the complex. We estimate $\Delta G^\ddagger$ for 2 to be in excess of 21 kcal/mol.

[12] Muetterties, E. L.; Pretzer, W. R.; Thomas, M. G.; Beier, B. F.; Thorn, D. L.; Day, V. W.; Anderson, A. B. *J. Am. Chem. Soc.* **1978**, *100*, 2090–2096.

[13] Wade, K., in ref 1, p 193.

[14] The reaction of 1 with $Fe_2(CO)_9$ in heptane at 40 °C for 3 h gave (μ_3-PhC_2CO_2-*i*-Pr)[$Fe(CO)_3Co(CO)_3NiCp$] in 85% yield as the only isolable product. This complex has been fully characterized spectroscopically and by X-ray crystallography. This reaction provides a new mode of access to heterotrimetallic pentanuclear clusters: Marinetti, A.; Jaouen, G.; Saillard, J. Y.; Mentzen, B.; Mutin, R.; Sayer, B. G.; McGlinchey, M. J., submitted for publication.

[15] (a) Geoffroy, G. L. *Acc. Chem. Res.* **1980**, *13*, 469–476. (b) Gladfelter, W. L.; Geoffroy, G. L. *Adv. Organomet. Chem.* **1980**, *18*, 207.

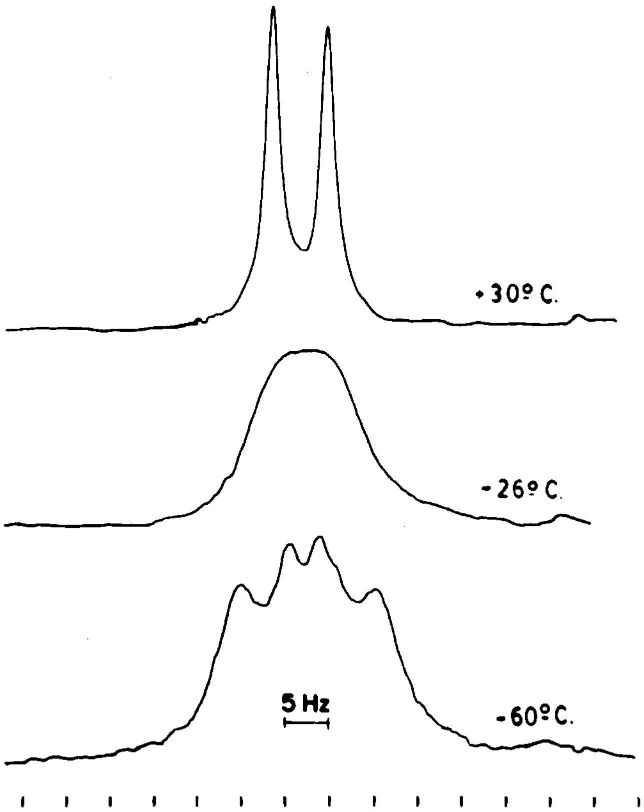
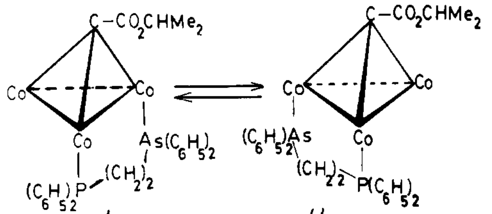


Figure 3. Temperature-dependent ^{1}H NMR spectrum (80 MHz) of 4 (4′) in CD_2Cl_2 (methyl region) showing interconversion of the enantiomers of 4. Carbonyls are omitted for clarity.

techniques.[16] A molecule which falls between these two extremes is (arphos)$Co_3C(CO)_7(CO_2CHMe_2)$ (4),[17] which



4 4′

again contains the diastereotopic probe. The appropriate section of the ^{1}H NMR spectrum is shown as Figure 3. This molecule, for which $\Delta G^{\ddagger} = 13.1 \pm 0.6$ kcal/mol for the racemization process, could utilize a mechanism involving cleavage of a Co–P or Co–As bond and migration of the dangling ligand with concomitant reorganization of the carbonyls. However, in light of the results in the M_2C_2 tetrahedral systems, it is conceivable that racemization could occur not only by ligand migration but also by direct interchange of the cluster skeletal nuclei. This and other related systems are currently under investigation using ^{59}Co NMR spectroscopy.

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(16) Gladfelter, W. L.; Geoffroy, G. L. *Inorg. Chem.* **1980**, *19*, 2579–2585.

(17) $Co_2(CO)_8$ (5.13 g) and CCl_3CO_2-*i*-Pr (1.75 g) in 50 mL of THF were heated for 3 h at 55 °C following the standard procedures (Seyferth, D. *Adv. Organomet. Chem.* **1976**, *14*, 97) to give $Co_3(CO)_9CCO_2$-*i*-Pr (2.9 g, 37%), mp 64–65 °C. This latter compound (0.35 g) and $Ph_2P(CH_2)_2AsPh_2$ (≡arphos) (0.22 g) in 35 mL of THF were heated at 50 °C for 1.5 h to give 4 (0.38 g), mp 176 °C, as black-green crystals after chromatography and crystallization from hexane/ether: ^{1}H NMR (80 MHz, CD_2Cl_2) δ 1.13 (d, $J = 6.25$ Hz at +30 °C); δ 1.12, 1.00 (dd at –60 °C); ^{13}C NMR (100.577 MHz, CD_2Cl_2, 22 °C) δ 243.1 (1 C), 205 (CO's exchanging at room temperature), 182.2 (CO_2), 137.7, 132.1, 130.5, 130.2, 129.2, 129.0, 128.9 (aromatics), 68.5 (*C*HMe$_2$), 25.4 (PCH_2, d, $J_{CP} = 23$ Hz), 23.1 ($AsCH_2$), 22.0 (CH*Me*$_2$); IR (CH_2Cl_2)ν_{CO} 2056 (s), 1998 (vs), 1975 (m), 1955 (sh), 1715 (s) cm^{-1}.

Acknowledgment. We thank the CNRS for financial support, Dr. C. A. Rodger, Bruker Spectrospin, Mississauga, Ontario, for the 250-MHz spectra, and Dr. R. E. Lenkinski, Southwest Ontario Regional NMR Center, Guelph, Ontario, for recording the 400-MHz spectra.

Registry No. 1, 79816-41-4; 2, 79839-04-6; 3, 79816-42-5; 4, 79816-43-6; $Co_2(CO)_8$, 10210-68-1; $(C_5H_5)_2Mo_2(CO)_6$, 12091-64-4; $Mn_2(CO)_{10}$, 10170-69-1; Cp_2Ni, 1271-28-9; $Co_3(CO)_9CCO_z$-$_i$-Pr, 36834-86-3.

Novel (Acetylene)molybdenum(II) Complexes, Mo(t-BuS)$_2$(t-BuNC)$_2$(RC≡CR′) (R, R′ = H or Ph)

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Received July 31, 1981

Summary: Several novel acetylene complexes of Mo(II), Mo(t-BuS)$_2$(t-BuNC)$_2$(RC≡CR′) (R, R′ = H or Ph), formally five-coordinate if the acetylene is counted as a monodentate ligand, are prepared from the reaction of Mo(t-BuS)$_2$(t-BuNC)$_4$ with acetylenes. The crystal structures of two of these were determined. The metal is in an approximate trigonal-bipyramid geometry, the acetylene CC vector parallel to the –N≡C—Mo—C≡N– axis of the trigonal bipyramid. This unusual orientation follows from the electronic structure of the complex.

Despite current interest in molybdenum thiolato complexes[1,2] viable synthetic materials have so far been rather limited.[1] The sulfur ligands in known (alkyne)molybdenum complexes, apart from $Mo(SC_6F_5)(\eta\text{-}C_5H_5)(CO)(CF_3C{\equiv}CCF_3)$,[3] are limited to dithiocarbamate[4-7] or similar chelating disulfur compounds such as $R_2PS_2^-$.[8] The

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(1) (a) Stiefel, E. I. *Prog. Inorg. Chem.* **1977**, *22*, 1–233. (b) Coucouvanis, D. *Ibid.* **1979**, *26*, 30–469. (c) Spence, J. T. In "Metal Ions in Biological Systems"; Sigel, H. Ed.; Marcel Dekker: New York, 1976; Vol. 5, pp 280–321.

(2) Newton, W. E.; Otsuka, S., Ed., "Molybdenum Chemistry of Biological Significance"; Plenum Press: New York, 1980.

(3) Howard, J. A. K.; Stanfield, R. F. D.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1976**, 246–250.

(4) Maata, E. A.; Wentworth, R. A. *Inorg. Chem.* **1979**, *18*, 524–526.

(5) Newton, W. E.; McDonald, J. W.; Corbin, J. L.; Ricard, L.; Weiss, R. *Inorg. Chem.* **1980**, *19*, 1997–2006.

(6) Ricard, L.; Martin, C., Weiss, R., XVII ICCC, Hamburg, 1976.

(7) Templeton, J. L.; Ward, B. C. *J. Am. Chem. Soc.* **1980**, *102*, 3288–3290.

(8) McDonald, J. W.; Corbin, J. L.; Newton, W. E. *J. Am. Chem. Soc.* **1975**, *97*, 1970–1971.