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Preparation of the Paramagnetic Hydrides $(Me_5C_5)_3M_3(\mu_3\text{-CH})(\mu\text{-H})$ (M = Ni, Co)

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Summary: MeLi reacts with $Me_5C_5M(acac)$ to give the trinuclear clusters $(Me_5C_5)_3M_3(\mu_3\text{-CH})(\mu\text{-H})$ (M = Co, Ni). The 49-electron nickel cluster is paramagnetic with one unpaired electron, and the 46-electron cobalt cluster is also paramagnetic; the latter reacts with dihydrogen to give diamagnetic $(Me_5C_5)_3Co_3(\mu_3\text{-CH})(\mu\text{-H})_3$.

Organometallic compounds of the d-block metals that have a methyl group bridging two identical metal centers, M(μ-Me)M, are rare.[1] The synthetic reaction for preparation of these dimetal compounds, whose electron counts range from 24 to 32 (not counting the electrons involved in the metal−metal bonds), is substitution of halide for methyl in otherwise identical compounds, protonation of bridging methylene precursors, or insertion of CH_2 into a metal hydride. In this paper, we show that the reaction of MeLi with (Me_5C_5)M(acetylacetonate) (M = Ni, Co)[2] does not give isolatable bridging methyls but instead gives trinuclear clusters, $(Me_5C_5)_3M_3(\mu_3\text{-CH})(\mu_3\text{-H})$, in which the methyne hydrogen and the hydride hydrogen atoms are derived from MeLi, explicitly in the case of M = Ni.

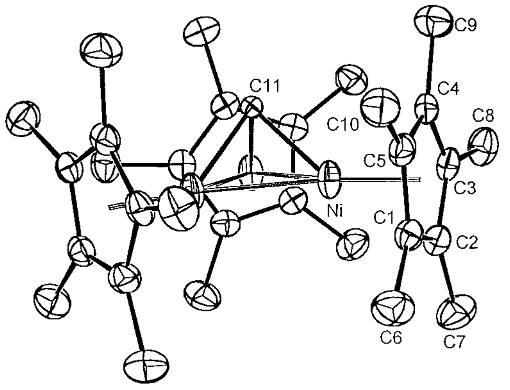

Figure 1. ORTEP diagram of $(Me_5C_5)_3Ni_3(\mu_3\text{-CH})(\mu\text{-H})$. The nickel and cobalt clusters are isostructural, and only the drawing for the nickel cluster is shown. For Co, the μ_3-CH hydrogen was located and refined in the major isomer only, but this hydrogen was not found in the nickel cluster.[4] The hydride hydrogens were not located in either of the clusters. The important bond lengths (Å) and angles (deg) are as follows, with nickel values given first and cobalt ones second: M−M = 2.415(1), 2.439(1); M−C(Cp)(av) = 2.135(6), 2.118(5); M−Cp(centroid) = 1.76, 1.73; M−C(11) = 1.913(7), 1.856(4); M−C(11)−M = 78.26(3), 82.10(3); Cp(centroid)−M−C(11) = 138, 138.

Addition of 1 molar equiv of MeLi to (Me_5C_5)Ni(acac) in diethyl ether at 0 °C gives a brown suspension from which brown prisms of $(Me_5C_5)_3Ni_3(\mu_3\text{-CH})(\mu\text{-H})$ can be crystallized from pentane in 60% yield.[3a] Figure 1 shows an ORTEP diagram; due to μ_3-CH, μ-H disorder these hydrogen atoms were not located.[4a] The presence of the bridging methyne and hydride ligands was established spectroscopically. The empirical composition was established by mass spectroscopy at low and high resolution; the observed molecular ion is nearly identical with that of the simulated molecular ion envelope (Figure 2a). The cluster is a 49-electron cluster and is isoelectronic with the Fischer−Palm cluster $Cp_3Ni_3(\mu_3\text{-CO})_2$.[5] In solution, the molecule has one unpaired electron; $\mu = 1.77\ \mu_B$ per cluster in C_6D_6 at 30 °C. In the solid state, χ_m^{-1} is linear from 5 to 300 K, giving $\mu = 1.93\ \mu_B$ ($\Theta = -8.23$ K) at 5 kG and $\mu = 1.83\ \mu_B$ ($\Theta = -4.28$ K) at 40 kG. In methylcyclohexane solution, the room-temperature EPR spectrum consists of a single line at $g = 2.046$, and the lower temperature spectrum (91 K, frozen glass) is axial with $g_\perp = 2.114$ and $g_\parallel = 2.009$. These values are nearly identical with those observed in $Cp_3Ni_3(\mu_3\text{-CO})_2$ and related 49-electron nickel clusters, implying that the HOMO in all cases has a single electron in an a′₂ (D_{3h} symmetry) symmetry orbital. [5] The origin of the μ_3-CH and μ-H ligands is MeLi, since use of CD_3Li gives $(Me_5C_5)_3Ni_3(\mu_3\text{-CD})(\mu$-

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(3) (a) $(Me_5C_5)_3(Ni_3)(\mu_3\text{-CH})(\mu\text{-H})$: The compound did not melt to 330 °C. IR: 2715 (m), 1435 (sh), 1371 (s), 1261 (w), 1155 (m), 1065 (m), 1023 (s), 981 (m), 943 (w), 819 (s), 612 (w), 390 (m), 354 (s) cm^{-1}. EIMS, low resolution reported as ion *m*/*e* (observed intensity, calculated intensity): 593 (83, 86); 594 (29, 40); 595 (100, 100); 596 (38, 41); 597 (56, 54); 598 (21, 21); 599 (22, 21); 600 (8, 8); 601 (7, 6). EIMS, high resolution: calcd 593.1738 ($^{58}Ni_3$), 595.1693 ($^{58}Ni_2{}^{60}Ni$); found 593.1725, 595.1681. Anal. Calcd for $C_{31}H_{47}Ni_3$: C, 62.5; H, 7.95. Found: C, 62.9; H, 7.95. (b) $(Me_5C_5)_3Co_3(\mu_3\text{-CH})(\mu\text{-H})$: the compound did not melt to 330 °C. IR: 2713 (m), 1409 (sh), 1371 (s), 1290 (w), 1158 (m), 1066 (m), 1024 (s), 976 (w), 946 (w), 900 (m), 856 (m), 834 (s), 609 (w), 539 (m), 487 (m), 409 (m), 371 (m) cm^{-1}. No distinct molecular ion was observed in the EIMS; instead, a broad envelope approximately 20 amu wide centered at 600 amu was observed. Anal. Calcd for $C_{31}H_{47}Co_3$: C, 62.4; H, 7.94. Found: C, 62.6; H, 7.94. The compound does not give a ^1H NMR spectrum at 28 °C. (c) Mp: 297 °C. IR: 2713 (w), 1675 (m), 1407 (sh), 1357 (m), 1261 (m), 1186 (m), 1156 (w), 1098 (w), 1068 (w), 1022 (s), 942 (w), 854 (m), 832 (s), 804 (m), 732 (w), 611 (m), 557 (m), 541 (m), 413 (m), 401 (m) cm^{-1}. EIMS $(M - H_2)^+$: *m*/*e* 596 (100, 100); 597 (34, 34); 598 (7, 6). Anal. Calcd for $C_{31}H_{49}Co_3$: C, 62.2; H, 8.25. Found: C, 62.2; H, 8.42.

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D), identified by a low-resolution mass spectrum that is shifted two units to higher mass relative to the unlabeled isotopomer (Figure 2b). Isolation of the deuterated species allows the infrared spectrum to be assigned; the two features at 2164 and 682 cm^{-1} are due to $\nu(Ni_3(\mu_3\text{-}CD))$ and $\nu(Ni_3(\mu_3\text{-}D))$, respectively. These features correspond to $\nu(Ni_3(\mu_3\text{-}CH))$, which is not observed, since it is hidden within the C−H modes at *ca.* 3000 cm^{-1}, and $\nu(Ni_3(\mu_3\text{-}H))$, which is observed at 981 cm^{-1}. The low value of the hydride stretching frequency is consistent with a triply bridging hydride.[6] The triply bridging hydride is presumably sitting on the C_3 axis on the face opposite that of the capping μ_3-CH ligand.

The cobalt compound $(Me_5C_5)Co(acac)$ behaves similarly, with MeLi giving black prisms of $(Me_5C_5)_3Co_3(\mu_3\text{-}CH)(\mu\text{-}H)$ in 60% yield from pentane (Figure 1).[3b,4b] The characterization of the cobalt cluster is more difficult than for its nickel analog, since no direct evidence for

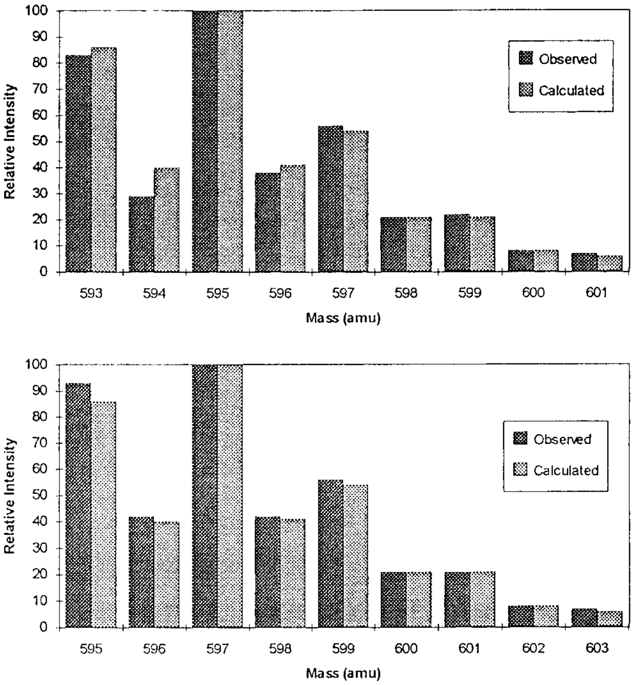

Figure 2. (a) Molecular ion envelopes for (a, top) $(Me_5C_5)_3Ni_3(\mu_3\text{-}CH)(\mu\text{-}H)$ and (b, bottom) $(Me_5C_5)_3Ni_3(\mu_3\text{-}CD)(\mu\text{-}D)$.

the hydride is obtained. The mass spectrum does not give a definitive molecular ion but rather an envelope of peaks. Although it is an even-electron cluster, it is paramagnetic, with a magnetic moment of 2.28 μ_B per cluster in C_6D_6 at 30 °C. The solid-state magnetic moment is temperature-dependent, since the plot of χ_m^{-1} relative to temperature is curved. At low temperature (5−50 K) $\mu = 2.41\ \mu_B$ ($\Theta = -0.03$ K) and from 160 to 300 K $\mu = 2.73\ \mu_B$ ($\Theta = -40.7$ K) per cluster at 5 kG; the values at 40 kG are identical. Thus, the 46-electron cluster is paramagnetic and the magnetic moment is slightly temperature dependent, perhaps due to lifting of the orbital degeneracy in the ^3A ground state at low temperature. The cobalt cluster is silent in the EPR spectrum as a frozen glass in methylcyclohexane down to 1.8 K. However, doping the paramagnetic cluster into the solid $(Me_5C_5)_3Co_3(\mu_3\text{-}CH)_2$, which is diamagnetic and isostructural with it,[4c] allows the observation of two broadened resonances at 1.7 K at $g = 2.157$ and 4.268. The latter feature is the "forbidden" half-field resonance expected for a ^3A ground state. This is consistent with the extensive experimental results that show the degenerate e″ orbitals, in D_{3h} symmetry, are half-occupied.[7] The question of the origin of the methyne and hydride groups in $(Me_5C_5)_3(Co_3)(\mu_3\text{-}CH)(\mu_3\text{-}H)$ cannot be answered unequivocally, since this cluster does not yield a well-defined molecular ion, and neither does its

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(4) (a) $(Me_5C_5)_3\ Ni_3\ (\mu_3\text{-}CH)(\mu\text{-}H)$ crystallizes in the trigonal space group $R\bar{3}$ with cell dimensions (−92 °C) $a = 11.556(2)$ Å, $\alpha = 100.40(2)°$, and $V = 1456.1(12)$ $Å^3$ with $Z = 2$. The data were collected on a Nonius CAD4 automated diffractometer with Mo Kα X-rays ($\lambda = 0.710\ 73$ Å) at −92 °C. The structure was solved from Patterson and electron density maps, after the nickel atoms were located by direct methods (SHELXS). All non-hydrogen atoms were refined anisotropically, except for the μ_3-C atom, since this atom was disordered on either side of the triangle of nickel atoms with an approximate occupancy ratio of 3:2. A difference Fourier map revealed the position of the hydrogen atoms on the Me_5C_5 ring. These atoms were placed in calculated positions and included in the structure factor calculations but not refined. All hydrogen atoms were given isotropic thermal parameters 1.3 times the *B*(iso) value of the atom to which they are attached. The positions of the methylidyne hydrogen and hydride hydrogen were masked by the disorder of the methylidyne carbon atom and were not included in the structure solution. Final refinement of the 104 variables using 1354 data for which $F_o^2 > 3\sigma(F_o^2)$ gave $R = 0.0369$ and R_w=0.0532. (b) $(Me_5C_5)_3Co_3(\mu_3\text{-}CH)(\mu\text{-}H)$ also crystallizes in the trigonal space group $R\bar{3}$ with cell dimensions (−98 °C) $a = 11.561(2)$ Å, $\alpha = 100.53(2)°$, and $V = 1455.9(14)$ $Å^3$ with $Z = 2$. The coordinates of the cobalt atoms were determined by direct methods (SHELXS), and the non-hydrogen atoms were determined by Fourier techniques and refined by least-squares methods, anisotropically. The μ_3-C atom was disordered on either side of the tricobalt plane with an approximate occupancy ratio of 3:1. A difference Fourier map revealed the positions of the hydrogen atoms on Me_5C_5 and μ_3-CH (major site only). These atoms were placed in calculated positions and included in the structure factor calculations but not refined. All hydrogens were given isotropic thermal parameters 1.3 times the *B*(iso) value of the atom to which they are bonded. The position of the hydride hydrogen was masked by the disorder, and its position was not included in the structure solution. Final refinement of 105 variables using 1041 data for which $F_o^2 > 3\sigma(F_o^2)$ gave $R = 0.0410$ and $R_w = 0.0540$. (c) $(Me_5C_5)_3Co_3(\mu_3\text{-}CH)_2$: To a solution of $(Me_5C_5)_3Co_3(\mu_3\text{-}CH)(\mu\text{-}H)$ (0.07 g, 0.1 mmol) in toluene (50 mL) was added 11.5 μL of CCl_4 (0.1 mol). Upon mixing, the solution very gradually changed color from black to red-purple and a black precipitate settled out. After the mixture was stirred at room temperature for 24 h, the volatile materials were completely removed under reduced pressure and the residue was extracted with pentane (65 mL). The red-purple solution was filtered, and the filtrate was concentrated to ca. 15 mL. Cooling to −80 °C afforded purple prisms for a total yield of 0.02 g (0.03 mmol, 27% yield). The compound did not melt to 330 °C. IR: 2714 (m), 1687 (s), 1484 (sh), 1406 (w), 1371 (s), 1160 (m), 1069 (m), 1024 (m), 989 (w), 945 (w), 906 (w), 856 (s), 836 (w), 611 (w), 570 (w), 538 (s), 450 (w), 409 (s) cm^{-1}. ^1H NMR (C_6D_6, 293 K, 90 MHz): δ 16.99 (s, 2H, μ_3-C*H*), 1.74 (s, 45H, C_5Me_5). EIMS: *m*/*e* 608 (100, 100); 609 (36, 36); 610 (7, 6). Anal. Calcd for $C_{32}H_{47}Co_3$: C, 63.2; H, 7.78. Found: C, 63.3; H, 8.02. $(Me_5C_5)_3Co_3(\mu_3\text{-}CH)_2$ crystallizes in the trigonal space group $R\bar{3}$ with cell dimensions (−83 °C) $a = 11.500$ (1) Å, $\alpha = 100.13(1)°$, and $V = 1439.9(7)$ $Å^3$ with $Z = 2$. The coordinates of the cobalt atoms were determined by direct methods (SHELXS). The non-hydrogen atoms were determined by Fourier techniques and refined by least-squares methods. All non-hydrogen atoms were refined anisotropically. A difference Fourier map revealed the positions of all hydrogen atoms, and these were included in the structure refinement. Final refinement of the 169 variables using the 1409 data for which $F_o^2 > 3\sigma(F_o^2)$ gave $R = 0.0267$ and $R_w = 0.033$.

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reaction product with H_2. Since these functional groups were derived from MeLi in the nickel cluster, we assume they were derived in a similar way in the cobalt cluster. A related series of tricobalt compounds with ethylidyne capping ligands has recently been prepared, viz., $(Me_5C_5)_3(Co_3)(\mu_3\text{-CMe})(X)$, where $X = \mu_3\text{-H}$, $\mu_3\text{-CMe}$, $\mu_2\text{-H}_3$.[8] The spectroscopic information that is available suggests that these two series have similar molecular structures.

Although the nickel cluster does not react with dihydrogen at 25 °C at 10 atm for periods of up to 1 week, the cobalt cluster slowly adds dihydrogen to give diamagnetic $(Me_5C_5)_3Co_3(\mu_3\text{-CH})(\mu_2\text{-H})_3$.[3c] The infrared spectrum shows a medium-intensity absorption at 1675 cm^{-1} consistent with bridging hydrides, $Co(\mu_2\text{-H})Co$.[6b,d] The ^1H NMR spectrum at 20 °C consists of three singlets at δ 16.9, 1.77, and −32.1 in an area ratio of 1:45:3, corresponding to the methyne, pentamethylcyclopentadienyl, and hydride resonances, respectively.

The crystal structures of the tricobalt and trinickel compounds are isomorphous, so that comparisons between the bond lengths are informative about the differences in their electronic structures. Both compounds have their metal atoms in identical oxidation states (7/3) and coordination numbers. The only difference is that the cobalt compound has three fewer electrons than nickel. The symmetry orbitals for trinuclear clusters have been extensively studied when the capping ligands are π-acceptors, such as CO, and π-donors, such as S.[5,7,9] Assuming that the frontier orbitals are similar when the capping ligands are methyne and hydride yields results that are in agreement with the magnetic susceptibility and EPR data presented above. The HOMO in the tricobalt cluster is a half-filled e″ set (in D_{3h} symmetry) that is composed predominantly of out-of-plane metal d_{xz} and d_{yz} orbitals that are metal−ring and metal−metal ligand antibonding. Proceeding from cobalt to nickel adds three electrons, two into the e″ orbital and one into the a'_2 orbital, which is predominantly composed of the in-plane metal d_{xy} orbital that is metal−metal antibonding. The expectation is that the averaged M−C(ring) and M−M distances will increase as three electrons are added to the cobalt cluster. As shown in Figure 1, the Ni−C(ring) and Ni−C(methyne) distances lengthen by 0.02 and 0.05 Å, respectively, but the Ni−Ni distance shortens by 0.02 Å. The shortening of the metal−metal bond length is not expected. Either a simple extension of the theory is inappropriate or other factors are involved, one of which is that for a given oxidation state and coordination number the radius of nickel is less than that of cobalt; Shannon estimates that Ni(II) in six-coordination is smaller than Co(II) by 0.05 Å.[10] If the latter explanation is correct, then the Ni−Ni distance did lengthen by 0.03 Å relative to its natural contraction. This observed contraction of the nickel−nickel distance forces the μ_3-CH cap farther away from the three nickel atoms that form the base of the equilateral triangle; this assumes that the CH/H disorder affects both structural parameters equally. If this rationalization is accepted, then the frontier orbitals derived for compounds such as $Cp_3M_3(\mu_3\text{-Co})_2$, where M = Co or Ni, can be used to qualitatively explain the electronic structure of the carbyne hydrides described here.

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Supporting Information Available: Tables giving full X-ray crystallographic data, bond lengths and angles, anisotropic thermal parameters, and positional parameters and text giving a complete discussion of how the structures were solved (27 pages). Ordering information is given on any current masthead page.

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