Tris(.eta.5-cyclopentadienyl)(.mu.3-alkylidyne)trinickel clusters: preparation, characterization, and molecular structure

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a dark red solution. After the solution was cooled to room temperature, the solvent was removed on a rotary evaporator followed by chromatography on silica gel. With hexane as eluent, a yellow band of unreacted $Ru_3(CO)_{12}$ (22 mg) was eluted followed by an orange band of unreacted **4** (28 mg) and a yellow band of an uncharacterized species (10 mg). When the polarity of the eluent was changed by the gradual addition of CH_2Cl_2, an orange band of **2** (10 mg, 28% based on consumed **4**) eluted when hexane/CH_2Cl_2 = 7:3 and a yellow band of **3** (5 mg, 13%) eluted at hexane/CH_2Cl_2 = 2:3 from which **4** was isolated as a dark orange solid by solvent evaporation. **3**: IR (CH_2Cl_2) ν_{CO} 2058 (w), 2033 (vs), 2017 (s), 1977 (m), 1956 (w), 1831 (w, br) cm^{-1}; MS (FD), *m/z* 1344 (M^+, ^{102}Ru); ^{13}C NMR (THF, −50 °C) δ 196.08, 201.47, 201.62, 202.62, 235.26, (1:2:2:2:1 intensity ratio). Anal. Calcd for $C_{28}H_{10}O_{16}N_2Ru_6$: C, 25.00; H, 0.74. Found: C, 25.26; H, 0.63.

Reaction of $Ru_6(\mu_4\text{-}NPh)_2(CO)_{15}$ (2) with $Ru_3(CO)_{12}$. A solution of **2** (60 mg, 0.050 mmol) and $Ru_3(CO)_{12}$ (30 mg, 0.047 mmol) in octane (40 mL) was refluxed for 10 h under N_2 to give a dark red solution. After the solution was cooled to room temperature the solvent was removed by rotary evaporation. Column chromatographic separation (SiO_2, hexane/CH_2Cl_2 eluent with a gradual increase in CH_2Cl_2 from 0% to 50%) gave a yellow band of $Ru_3(CO)_{12}$ (2 mg) followed by a trace amount of an unidentified dark yellow band and then a yellow band of **3**. The latter was isolated in 57% yield (25 mg) by solvent evaporation.

X-ray Diffraction Study of $Ru_6(\mu_4\text{-}NPH)_2(CO)_{15}\cdot CH_3C({=}O)CH_3$ (2). *Table I contains the crystal and refinement parameters for* **2**. A deep red crystal of **2** was grown from acetone and mounted on a glass fiber. Systematic absences in the diffraction data uniquely defined the space group, $P2_1/c$. The unit cell parameters were obtained from the least-squares fit of the angular settings of 25 reflections (21° ≤ 2θ ≤ 26°). An empirical correction for absorption was applied to the reflection data (216 Ψ-scan data; six-parameter, pseudoellipsoid model, T_{max}/T_{min} = 0.430/0.338). The merging *R* factor for the Ψ-scan data was reduced from 4.4% to 1.6%. Corrections were also applied for a linear 3% decay in standard reflection intensity.

The six Ru atoms were located by an interpreted Patterson routine; the remaining non-hydrogen atoms were located from subsequent difference Fourier syntheses. A thermally active and/or partially disordered molecule of acetone was found cocrystallizing with **2**. Occupancy refinement of the acetone molecule suggested possible substoichiometric occupancy [sof = 0.78 (1)] (*D*(calcd) was determined by assuming a sof of 1.0). All non-hydrogen atoms were anisotropically refined, and all hydrogen atoms were treated as idealized, updated isotropic contributions (*d*(CH) = 0.96 Å). SHELXTL (5.1) software was used for all computations (Nicolet Corp., Madison, WI).

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Supplementary Material Available: Tables of isotropic thermal parameters, complete bond lengths and angles, and calculated hydrogen atom positions (7 pages); a listing of structure factors (32 pages). Ordering information is given on any current masthead page.

Tris(η^5-cyclopentadienyl)(μ_3-alkylidyne)trinickel Clusters: Preparation, Characterization, and Molecular Structure

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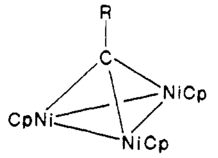
Tris(η^5-cyclopentadienyl)(μ_3-alkylidyne)trinickel clusters $(CpNi)_3(\mu_3\text{-}CR)$ (R = CH_3 (**1**), C_2H_5 (**5**), $CH(CH_3)_2$ (**6**)) with a tetrahedral Ni_3–(μ_3-C) core have been synthesized by reaction of nickelocene (Cp_2Ni) with methyl- or vinyllithium (to give **1**), with $BrMgCH{=}CHCH_3$ (to give **5**), or with $BrMgCH{=}C(CH_3)_2$ (to give **6**). CpNiCp* (Cp* = C_5Me_5) reacts with methyllithium unselectively to give a mixture of $(Cp_nCp^*_{3-n}Ni_3)CCH_3$ (**2**–**4**) with *n* = 2, 1, and 0, respectively. The molecular structure of **1** has been determined by single-crystal X-ray techniques. Crystal data: *a* = 11.684 (3) Å, *b* = 14.142 (2) Å, *c* = 9.361 (2) Å; *V* = 1546.8 Å^3; *T* = 293 K; orthorhombic; *Pnma*; *Z* = 4, D_{calcd} = 1.71 g cm^{-3}; λ(Mo Kα) = 0.71069 Å; final *R* = 0.032 (*wR* = 0.033) for 1567 unique observed reflections.

Although, the (μ_3-alkylidyne)tricobalt clusters have been investigated in detail, the analogous (μ_3-alkylidyne)trinickel compounds have received little attention. Ustynyuk et al.[1] obtained $(\eta^5\text{-}CpNi)_3CPh$ from the reaction of nickelocene with benzylmagnesium halide and proposed structure A (R = Ph) on the basis of ^1H NMR, MS, and IR data.



A

Similar reactions of Cp_2Ni with neopentyl- or ((trimethylsilyl)methyl)lithium have been used by Booth and Casey[2] to prepare the clusters $(CpNi)_3CR$ (R = CMe_3, $SiMe_3$). Recently, Vahrenkamp et al.[3] described the preparation and the molecular structure of a trinickel cluster A (R = CO_2Me). In none of these reactions does R contain α-hydrogen atoms. Reactions of Cp_2Ni with RCH_2M (M = Li, MgX), in which R contains α-H atoms (R = Me, Et, Pr), result in the decomposition of the unstable $CpNiCH_2R$ intermediate mainly via β-H elimination, and no (μ_3-alkylidyne)trinickel clusters of the

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‡ Junior Research Fellow of the Max-Planck-Gesellschaft in 1987.

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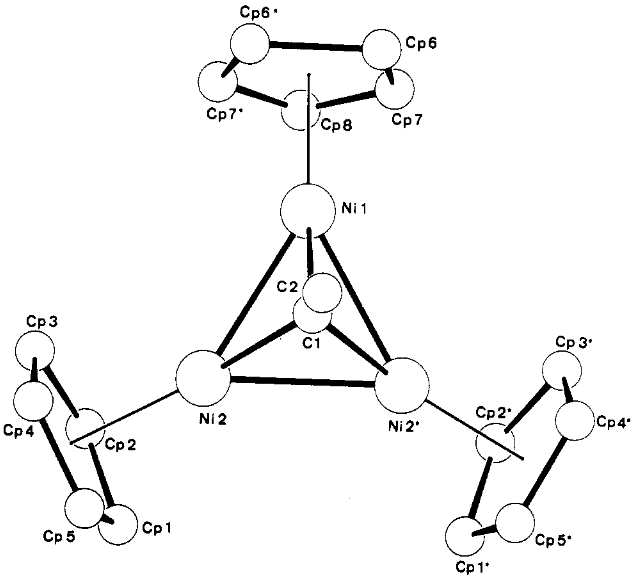

Figure 1.

Table I

cell data: $a = 11.684$ (3), $b = 14.142$ (2), $c = 9.361$ (2) Å
orthorhombic, *Pnma*
black prisms from toluene/pentane
crystal size: 0.17 × 0.20 × 0.70 mm
2561 intensity data ($0 < h < 13$, $0 < k < 16$, $0 < l < 19$)
θ_{max}: $1.44 < \theta < 29.91°$
Enraf–Nonius CAD4
graphite-monochromated Mo Kα X-radiation
total of 2315 unique measured intensities, $1567 I > 2.0\sigma(I)$, heavy-atom method
full-matrix least squares
$R = 0.032$ ($wR = 0.033$) for 135 variables and 1567 reflections
EOF = 1.64
$\Delta/\sigma = 0.97$.
residual density: ±0.54 e $Å^{-3}$ of the Ni atom.

Table II. Selected Interatomic Distances (Å) and Angles (deg) with Esd's in Parentheses

Bond Distances			
Ni1–Ni2	2.325 (1)	C1–C2	1.494 (8)
Ni2–Ni2*	2.349 (1)	Ni1–D2[a]	2.082 (6)
Ni1–C1	1.840 (4)	Ni2–D1	2.121 (4)
Ni2–C1	1.836 (1)	C–C in Cp(av)	1.385 (33)
Bond and Interplanar Angles			
Ni1–Ni2–Ni2*	59.7 (1)	C2–C1–Ni2	134.2 (1)
Ni2–Ni1–Ni2*	60.7 (1)	C2–C1–Ni1	130.1 (4)
Ni1–C1–C2	130.1 (4)	C1–Ni2–Ni1	50.8 (1)
Ni2–C1–C2	134.2 (1)	Ni1,Ni2,Ni1*/Cp1–Cp5	107.9
Ni1–C1–Ni2	78.5 (2)	Ni1,Ni2,Ni1*/Cp6–Cp8	102.9
Ni2–C1–Ni2*	79.5 (1)	Cp1–Cp5/Cp6–Cp8	109.7
		Cp1–Cp5/Cp1*–Cp5*	117.7

[a] D1 and D2 are the midpoints of the Cp rings.

$(CpNi)_3CR$ type (R = Me, Et, Pr) could be isolated.[2,4]

Results and Discussion

In the course of our investigations of the synthesis[5-8] and the chemical behavior[5,8-10] of η^2-alkene complexes of CpNi organyls, we observed that Cp_2Ni reacts with methyllithium in THF and in the absence of a coordinating olefin to give, among other products, the (μ_3-ethylidyne)trinickel cluster **1**. Pure **1** was isolated in 10–15% yield (eq 1).

$$4CH_3Li + 3Cp_2Ni \xrightarrow[-CpLi,-\ CH_4]{0\text{-}20\ °C} \underset{1}{(CpNi)_3(\mu_3\text{-}CCH_3)} \qquad (1)$$

Previously,[2] it had been claimed that no products whatsoever could be identified from this reaction. In addition to **1**, at least one further compound of the analytical composition $(CpNi)_3CH$, but of unknown structure,[4] is formed, as well as clusters with more than three CpNi fragments. These multinuclear clusters will be the subject of further investigations.

1 sublimes at 60 °C (0.001 Torr), melts without decomposition at 158–160 °C, and oxidizes easily in air but is not hydrolyzed by water. The mass spectrum shows a parent peak at m/z 396 (^{58}Ni). The ^{13}C NMR spectrum of **1** established the presence of the μ_3-ethylidyne carbon atom[11] at δ 289.3 (s).

The mixed nickelocene derivative CpNiCp* (Cp* = C_5Me_5) reacts with methyllithium (molar ratio 1:1.5) unselectively to give a mixture of $(Cp_nCp^*_{3-n}Ni_3)C\text{-}CH_3$ clusters (**2**:n = 2; **3**:n = 1; **4**:n = 0). **2**–**4** could not be separated chromatographically, but **2** and **3** could be removed from the mixture by sublimation at 60–90 °C in vacuo; the solid residue was pure **4**.

The molecular structure of **1** is shown in Figure 1, experimental details and a selection of distances and angles are given in Tables I and II. As demanded by the crystallographic site symmetry (*Cs*—*m*) of the space group *Pnma*, the structure of **1** contains a mirror plane through Ni1, C1, C2 and bisecting one of the Cp rings. The metal triangle is defined by two slightly different metal–metal distances. Inspection of intramolecular contacts reveals that the elongation of Ni2–Ni2* by 0.024 Å is due to steric crowding of the Cp rings at these atoms. As a result, the C2 atom at the apical methylidyne carbon atom C1 is tilted slightly toward the Ni1 atom. All relevant distances as given in Table II are similar to reported values.[3,12,13] The three Ni–Cp (centroid) distances average 1.80 Å, while the 15 Ni–C(ring) distances average 2.16 Å.

A more general method for the synthesis of (μ_3-alkylidyne)trinickel clusters is the reaction of nickelocene with vinyl or β-substituted vinyl derivatives of lithium or magnesium halide in THF at room temperature (eq 2).

The products were obtained in low to moderate yields by chromatography and crystallization: **1**, 6%; **5**, 60%; **6**, 23%. The ^{13}C NMR spectra establish the presence of the μ_3-alkylidyne carbon atoms at δ 283.3 (**5**) and 303.8 (**6**). In the mass spectra, the natural abundances of the ^{58}Ni and ^{60}Ni isotopes indicate the presence of three nickel atoms in the molecule.

For the reaction pathway, we assume that in the first step of reaction 2 a Cp and the vinylic ligand are exchanged between Ni and Li or Mg to give CpNi(vinyl). This 16-electron intermediate can be trapped by coordination to

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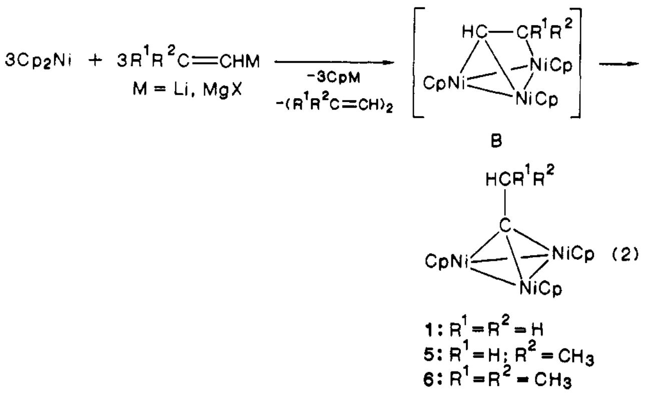

1: $R^1 = R^2 = H$
5: $R^1 = H$; $R^2 = CH_3$
6: $R^1 = R^2 = CH_3$

an ethylene molecule[7,14] and isolated as an η^2-ethylene complex in the case of Cp*[14] or identified as the ethylene insertion product $CpNiCH_2CH_2CH{=}CH_2$.[7] In the absence of a coordinating olefin the CpNi(vinyl)moieties may associate to give, after reductive elimination of two vinyl ligands, the intermediate B and the 1,3-diene $R^1R^2C{=}CHCH{=}CR^1R^2$. B rearranges by hydrogen migration from the α- to the β-carbon atom with simultaneous formation of the μ_3-C–Ni bond.

Experimental Section

All manipulations were carried out under an atmosphere of argon. The NMR spectra were recorded with either a Bruker AM-200 FT (^{1}H NMR) or a WM-300 FT (^{13}C NMR) spectrometer. The spectra were referenced indirectly to TMS via residual solvent signals. ^{1}H NMR: THF-d_8, δ 3.58; toluene-d_8, δ 2.09. ^{13}C NMR: THF-d_8, δ 25.28; toluene-d_8, δ 20.43; benzene-d_6, δ 128.06.

Preparation of (η^5-CpNi)$_3$(μ_3-CCH$_3$) (1). To a solution of 17.6 mmol of Cp_2Ni in 80 mL of THF at 0 °C was added slowly 23.8 mmol of CH_3Li in 22 mL of ether. The mixture was allowed to warm to ambient temperature and was stirred for a further 3 h. Pentane (50 mL) was then added and the reaction mixture hydrolyzed with 100 mL of deoxygenated water. The separated organic layer was dried (molecular sieves 4A), and a dark green solid was obtained after distilling off the solvents in vacuo. The remaining solid was dissolved in 2 mL of toluene and chromatographed on a column (60 × 3 cm; packed with neutral Al_2O_3 (II–III) in hexane) with toluene–hexane (3:2) as eluent. A brown-red fraction was collected, and after evaporation of the solvents, the product was crystallized from a toluene–hexane mixture (1:2) to give 0.26 g (0.66 mmol, 11%) of 1 as dark red crystals. Anal. Calcd for $C_{17}H_{18}Ni_3$ (398.5): C, 51.24; H, 4.55; Ni, 44.20. Found: C, 51.35; H, 4.48; Ni, 44.10. Molecular weight (cryoscopic benzene): 388. ^{1}H NMR (toluene-d_8, 300 K): δ 5.12 (s, Cp, 15 H), 3.67 (s, CH_3, 3 H). ^{13}C NMR (benzene-d_6, 311 K): δ 289.3 (s, μ_3-C), 88.1 (d, Cp, $^1J_{C,H}$ = 174 Hz), 46.1 (q, CH_3, $^1J_{C,H}$ = 127 Hz).

(η^5-C$_5$Me$_5$Ni)$_3$(μ_3-CCH$_3$) (4). CH_3Li (14.0 mmol) in 15 mL of ether was added at ambient temperature to a stirred solution of 2.40 g (9.3 mmol) of (C_5Me_5)CpNi in 60 mL of THF. After 5 h the brown reaction mixture was worked up in the same manner as described for 1 and chromatographed with toluene–THF (3:2). A dark red fraction was collected, and after evaporation of the solvents there remained a mixture of 3 and 4 as a dark red solid, [(η^5-Cp)(η^5-C$_5$Me$_5$)$_2$Ni$_3$](μ_3-CCH$_3$) (3): ^{1}H NMR (toluene-d_8, 300 K): δ 4.99 (s, Cp, 5 H), 3.39 (s, CH_3, 3 H), 1.68 (s, CH_3 (Cp*), 30 H). 3 was removed by sublimation at 90 °C (10^{-4} Torr). Crystallization of the residue gave at −78 °C 0.9 g (1.5 mmol, 48%) of dark red crystals of 4. Anal. Calcd for $C_{32}H_{48}Ni_3$ (608.9): C, 63.13; H, 7.95; Ni, 28.93. Found: C, 62.80; H, 8.36; Ni, 28.83. ^{1}H NMR (200.1 MHz, toluene-d_8, 300 K): δ 3.36 (s, CCH_3, 3 H), 1.73 (s, CH_3 (Cp*), 45 H). MS (70 eV, 180 °C): m/z (relative intensity) (^{58}Ni) 606 (M$^+$, 25), 592 (15), 464 (15), 442 (100).

Preparation of (η^5-CpNi)$_3$(μ_3-CCH$_2$CH$_3$) (5). A solution of 14 mmol of $BrMgCH{=}CHCH_3$ in 15 mL of ether was added dropwise to a solution of 6.9 mmol of Cp_2Ni in 50 mL of THF at ambient temperature. After hydrolysis and extraction with hexane, the dried hexane solution was chromatographed. A red fraction was collected, and after evaporation of the solvent the residue was crystallized from ether. Black-red crystals of 5 (0.57 g, 60%) were obtained. Anal. Calcd for $C_{18}H_{20}Ni_3$ (412.5): C, 52.41; H, 4.89; Ni, 42.70. Found: C, 52.80; H, 4.86; Ni, 42.38. ^{13}C NMR (75.5 MHz, THF-d_8, 313 K): δ 298.0 (s, μ_3-C), 87.8 (d, Cp, $^1J_{C,H}$ = 174 ± 1 Hz), 50.8 (t, C-1 (ethyl), 19.8 (q, C-2 (ethyl). ^{1}H NMR (200.1 MHz, toluene-d_8, 300 K): δ 5.12 (s, Cp), 3.59 (q, $\mathit{CH_2}CH_3$), 1.61 (t, $CH_2\mathit{CH_3}$).

Preparation of (η^5-CpNi)$_3$(μ_3-CCH(CH$_3$)$_2$) (6). $BrMgCH{=}C(CH_3)_2$ (32 mmol) and 12.9 mmol of Cp_2Ni in 80 mL of THF at room temperature gave (after crystallization from hexane) 0.43 g (1.0 mmol, 23%) of dark red crystals of 6. Anal. Calcd for $C_{19}H_{22}Ni_3$ (426.5): C, 53.51; H, 5.20; Ni, 41.30. Found: C, 54.00; H, 5.25; Ni, 40.89. ^{13}C NMR (75.5 MHz, toluene-d_8, 313 K): δ 303.8 (s, μ_3-C), 87.7 (d, Cp), 52.3 (d, C-1 (isopropyl)), 28.1 (q, C-2 (isopropyl). ^{1}H NMR (200.1 MHz, toluene-d_8, 300 K): δ 5.12 (s, Cp), 3.48 (m, $\mathit{CH}(CH_3)_2$), 1.56 (d, $CH(\mathit{CH_3})_2$).

Supplementary Material Available: Tables of crystal data, fractional coordinates, thermal parameters, bond distances, and bond angles (5 pages); a listing structure factors (8 pages). Ordering information is given on any current masthead page.

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