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DICYCLOPENTADIENYLNICKEL: A PROBLEMATICAL REAGENT IN CLUSTER SYNTHESIS

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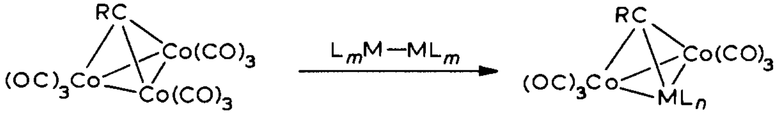
Summary

The room temperature reaction of $(C_5H_5)_2Ni$ with $Co_3(CO)_9CR$, where R is $CO_2CH(CH_3)_2$, gives almost quantitative replacement of a $Co(CO)_3$ group by a $(C_5H_5)Ni$ fragment. However, the same reagents in refluxing THF do not lead to further replacement of Co by Ni but instead yield the products $(C_5H_5)_3Co_3(CO)(H)CR$ and $(C_5H_5)_3Co_2Ni(CO)CR$ in which carbonyl groups have been replaced by cyclopentadienyl ligands. The isolobal nature of the fragments in these complexes is noted.

In recent years routes to heterometallic transition metal clusters [1–3] have advanced from the age of serendipity into the era of logical, controlled syntheses with some degree of mechanistic understanding; such developments are well exemplified by the work of Stone [4,5] and Vahrenkamp [6–8]. The latter has demonstrated that alkylidynetricobalt clusters can undergo exchange of organometallic fragments (ML_n) via substitution reactions as typified in Scheme 1.

SCHEME 1



ML_m = $CpMo(CO)_3$; $CpW(CO)_3$; $CpFe(CO)_2$; CpNi(CO)
ML_n = $CpMo(CO)_2$; $CpW(CO)_2$; CpFe(CO) ; CpNi
R = CH_3

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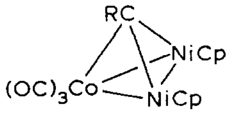
A rationale for the interchangeability of these fragments is provided by the idea of isolobality. This concept was recently reviewed by Hoffmann [9] and classified molecular fragments according to the number, symmetry, extent in space and electronic occupancy of their frontier orbitals. We see that the tricarbonylcobalt moiety, as well as all the other ML_n units above can provide three frontier orbitals and three electrons to the skeletal framework of the cluster. In the simplest isolobal terms, all of these molecules are analogous to tetrahedrane.

In the course of our investigations into the NMR fluxionality of transition metal clusters [10,11] we had need of the molecules **1** and **2**.



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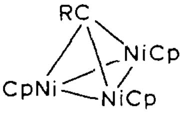


2

R = CO_2CHMe_2

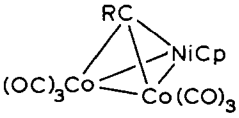
Although preparations of the trinickel cluster have been reported for R = $PhCH_2$, CMe_3 and $SiMe_3$ [12,13], no general route to this system appears to have been developed. Accordingly we chose to attempt a synthesis via the sequential replacement of $Co(CO)_3$ units by CpNi moieties. The facile synthesis of Cp_2Ni relative to that of $[CpNi(CO)]_2$, together with its earlier successful use to incorporate CpNi fragments into tetrahedral clusters [14], prompted us to treat $RCCo_3(CO)_9$ with Cp_2Ni. At ambient temperature in THF, replacement of one $Co(CO)_3$ unit by CpNi to give **3** proceeds readily, but it was clear that more forcing conditions would be required for multiple substitution to take place. However, when an excess of Cp_2Ni was heated under reflux in THF for several hours with the tricobalt cluster, two major products could be isolated.

One product showed a single carbonyl resonance at 1820 cm^{-1} in the infrared, and singlets in the ^1H NMR spectrum at δ 4.82 (15H) and -9.4 ppm (1H). These data, together with the mass spectrometric results allowed its identification as **4** which contains three CpCo moieties, a bridging carbonyl and a hydride. The molecule is, not surprisingly, fluxional and the hydride resonance occurs at a similar position to that reported by Geoffroy [15] for the related compound $HFeCo_2(CO)_9CR'$, **5** where $R' = CH_3$, C_2H_5, C_6H_5. (Only one of several fluxional structures of **5** is shown).

Similarly, the second product exhibited a bridging carbonyl resonance at 1810 cm^{-1}, two cyclopentadienyl resonances in the ratio 2/1 but no metal hydride signal. These data, together with the mass spectral fragmentation pattern, are consistent with the formulation as shown in **6** with two CpCo groups and a single CpNi fragment.

We note that the related molecules $Cp_2Co_3(CO)_4CCH_3$ and $(C_5Me_5)_2Co_3(CO)_4CCH_3$ have been prepared by heating the tricobalt-cluster under reflux in THF along with C_5H_6 or C_5Me_5H, respectively [16,17].

These results demonstrate the propensity of Cp_2Ni to decompose upon prolonged thermolysis to release cyclopentadienyl fragments which displace the labile carbonyl ligands on cobalt. Similar behaviour has been observed in the reactions of nickelo-



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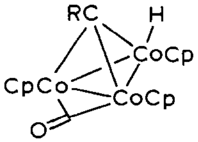

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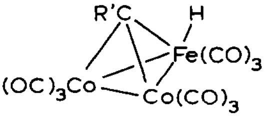

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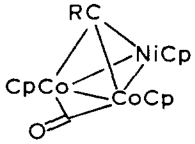

6

R = CO_2CHMe_2

cene with $Ni(CO)_4$ and $Fe(CO)_5$ to produce $Cp_2Ni_2(\mu\text{-}CO)_2$ and $Cp_2NiFe(CO)(\mu\text{-}CO)_2$, respectively [18,19]. In electron counting terms, three carbonyls are replaced by one cyclopentadienyl group and a hydrogen, while two cyclopentadienyl ligands account for five carbonyl groups. The compounds **3** through **6** provide nice examples of the isolobal relationships:

$$\mathrm{Co(CO)_3} \underset{\bigcirc}{\longleftrightarrow} \mathrm{NiCp} \underset{\bigcirc}{\longleftrightarrow} \mathrm{HFe(CO)_3} \underset{\bigcirc}{\longleftrightarrow} \mathrm{HCoCp}$$

To conclude, we find that Cp_2Ni is an excellent reagent for the introduction of a single CpNi fragment under mild conditions, but prolonged heating leads to extensive replacement of carbonyl groups by cyclopentadienyl ligands. Other examples of the incorporation of CpNi fragments into a variety of clusters will be reported later.

Experimental

All reactions were carried out under a dry nitrogen atmosphere. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Proton and ^{13}C NMR spectra were recorded in C_6D_6 solutions using a Bruker WP80 spectrometer. Infrared spectra were recorded on a Perkin–Elmer 283 instrument using KBr solution cells and cyclohexane as solvent. Mass spectrometry was performed on a VG micromass 7070 spectrometer equipped with a VG 2035 data system.

Preparation of $Co_3(CO)_9CCO_2CH(CH_3)_2$

Following the general procedure of Seyferth [20], $Co_2(CO)_8$ and CCl_3CO_2-i-Pr reacted to give the product in 40% yield. The crude product was recrystallized from petroleum ether/ether; m.p. 64–65°C, lit. [10] 64–65°C. The ^1H NMR spectrum showed a doublet at δ 1.34 (6H) and a septet at 5.27 ppm (1H), (J(HH) 6.3 Hz). The ^{13}C NMR spectrum showed peaks at δ 69.7 (CH) and 21.7 ppm (CH_3). The infrared spectrum exhibited ν(CO) at 2105m, 2075s, 2045s, 2025s, 1980w and 1690 (ester)

cm^{-1}. Major mass spectral peaks occured at m/z (%): 500, $C_{13}H_7Co_3O_{10}^+$,(2); 388, $C_9H_7Co_3O_6^+$,(2); 360, $C_8H_7Co_3O_5^+$,(4); 332, $C_7H_7Co_3O_4^+$,(2); 304, $C_6H_7Co_3O_3^+$,(1); 248, $C_4H_7Co_3O^+$,(2); 190, $CHCo_3^+$,(1); 59, Co^+,(100).

Reaction of $Co_3(CO)_9CCO_2CH(CH_3)_2$ with $(C_5H_5)_2Ni$

(a) At room temperature. To a solution containing 0.68 g (1.29 mmol) of $Co_3(CO)_9CCO_2CH(CH_3)_2$ in THF (50 cm^3) was added 0.55 g (2.91 mmol) of $(C_5H_5)_2Ni$, and the solution was stirred at room temperature for one week. Progress of the reaction was monitored by TLC (eluent, ether/petr. ether, 15/85; yellow spot Cp_2Ni, $R_F = 0.86$; greyish-purple spot $Co_3(CO)_9CCO_2CH(CH_3)_2$, $R_F = 0.80$ and dark brown spot $CpNiCo_2(CO)_6CCO_2CH(CH_3)_2$, $R_F = 0.65$). The solvent was removed in vacuo to yield a dark brown solid which was chromatographed on silica gel with ether/petr. ether (15/85) to give deep brown crystals of **3** (0.63 g, 1.24 mmol; 96%). The ^1H NMR spectrum showed a doublet at δ 1.30 (6H), a singlet at 4.99 (5H) and a septet at 5.27 ppm (1H), (J(HH) = 6.1 Hz). The ^{13}C NMR spectrum showed peaks at δ 22.5 (CH_3), 68.0 (CH) and 91.7 ppm (C_5H_5). The infrared spectrum exhibited ν(CO) at 2075m, 2040s, 2015s, 2000s and 1675 (ester) cm^{-1}. Major mass spectral peaks occurred at m/z (%): 508/510, $C_{16}H_{12}Co_2NiO_8^+$,(1); 480/482, $C_{15}H_{12}Co_2NiO_7^+$,(7); 452/454, $C_{14}H_{12}Co_2NiO_6^+$,(17); 424/426, $C_{13}H_{12}Co_2NiO_5^+$,(3); 396/398, $C_{12}H_{12}Co_2NiO_4^+$,(4); 368/370, $C_{11}H_{12}Co_2NiO_3^+$,(36); 340/342, $C_{10}H_{12}Co_2NiO_2^+$,(28); 312/314, $C_9H_{12}Co_2NiO^+$,(53); 254/256, $C_6H_6Co_2Ni^+$,(46); 189/191, $CHCo_2Ni^+$,(38); 188/190, CCo_2Ni^+,(100); 173/175, $C_2CoNiO_2^+$,(16); 123/125, $C_5H_5Ni^+$,(100).

(b) In refluxing THF. To a solution of $Co_3(CO)_9CCO_2CH(CH_3)_2$ (1.48 g, 2.80 mmol) in THF (50 cm^3) was added 1.90 g (10 mmol) of $(C_5H_5)_2Ni$. The resulting solution was heated under reflux overnight. Progress of the reaction was monitored by TLC and indicated the formation of five products. The solution was allowed to cool to room temperature, the solvent removed in vacuo and the residue chromatographed on silica gel. The first two bands were eluted with petr. ether, the next two with ether/petr. ether (15/85) and the final band with ether. Recrystallisation of the third band gave purple-black crystals of **4** (0.46 g, 0.92 mmol; 33%), and recrystallisation of the fourth band gave dark brown crystals (0.69 g, 1.39 mmol; 49%) of **6**.

The first, second and fifth bands were obtained only in minor amounts and have not been identified. The first band gave a light brown powder which gave no assignable IR or ^1H NMR peaks. The second band yielded a yellow-brown powder showing IR absorption at 1900, 1860 and 1855 cm^{-1}, but no ester carbonyl. ^1H NMR gave only a broad singlet centred at δ 5 ppm. The final band to be eluted gave a brown-black solid exhibiting IR absorption at 1790, 1765 and 1680 cm^{-1}. The ^1H NMR spectrum shows Cp resonances at δ 4.8, 4.9, 5.2 and 5.3 ppm and is certainly a mixture of several compounds. Presumably these complexes and others which could not be eluted from the column account for the remainder of the nickel from the starting material. The ^1H NMR spectrum of **4** showed a broad singlet at δ −9.4 (1H), a doublet at 1.41 (6H), a singlet at 4.82 (15H) and a septet at 5.55 ppm (1H) (J(HH) 6.2 Hz). The ^{13}C NMR spectrum showed peaks at δ 22.7 (CH_3), 67.8 (CH) and 88.7 ppm (C_5H_5). The infrared spectrum exhibited ν(CO) at 1820m and 1680 (ester) cm^{-1}. Major mass spectral peaks at m/z (%): 500, $C_{21}H_{23}Co_3O_3^+$,(4); 499, $C_{21}H_{22}Co_3O_3^+$,(8); 472, $C_{20}H_{23}Co_3O_2^+$,(2); 471, $C_{20}H_{22}Co_3O_2^+$,(3); 414, $C_{17}H_{17}Co_3O^+$,(2); 413, $C_{17}H_{16}Co_3O^+$,(4); 386, $C_{16}H_{17}Co_3^+$,(4); 385,

$C_{16}H_{16}Co_3^+$,(14); 370, $C_{11}H_{13}Co_3O_3^+$,(8); 369, $C_{11}H_{12}Co_3O_3^+$,(3); 305, $C_6H_8Co_3O_3^+$,(7); 304, $C_6H_7Co_3O_3^+$,(4); 246, $C_3HCo_3O_2^+$,(8); 190, $C_{10}H_{11}Co^+$,(10); 189, $C_{10}H_{10}Co^+$,(100); 125, $C_5H_6Co^+$,(5); 124, $C_5H_5Co^+$,(78); 66, $C_5H_6^+$,(25); 65, $C_5H_5^+$,(15); 59, Co^+,(24).

The ^1H NMR spectrum of **6** showed a doublet at δ 1.46 (6H), singlets at 4.89 (10H) and 5.09 (5H) and a septet at 5.55 ppm (1H) (J(HH) 6.2 Hz). The ^{13}C NMR spectrum showed a peaks at δ 23.1 (CH_3), 68.2 (CH), 86.7 (C_5H_5Co) and 91.0 ppm (C_5H_5Ni). The infrared spectrum exhibited ν(CO) at 1810 m and 1680 (ester) cm^{-1}. Major mass spectral peaks occurred at m/z (%): 498/500, $C_{21}H_{22}Co_2NiO_3^+$,(25); 470/472, $C_{20}H_{22}Co_2NiO_2^+$,(9); 412/414, $C_{17}H_{16}Co_2NiO^+$,(5); 384/386, $C_{16}H_{16}Co_2Ni^+$,(41); 371/373, $C_{15}H_{15}Co_2Ni^+$,(8); 190, $C_{10}H_{11}Co^+$,(11); 189, $C_{10}H_{10}Co^+$,(100); 124, $C_5H_5Co^+$,(10); 123/125, $C_5H_5Ni^+$,(4).

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