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Synthesis and X-ray Structure of $Co_3(CO)_9[CC(O)OCHC]Co_2Fe(CO)_9$, an Unexpected Product of the Reaction of $[PPh_4][HFe(CO)_4]$ with $[Co_3(CO)_9CCO][PF_6]$

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$[Co_3(CO)_9CCO][PF_6]$ reacts at room temperature with $[PPh_4][HFe(CO)_4]$ to give the complex $Co_5Fe(CO)_8[CC(O)OCHC]$ as the main product of the reaction (20% yield). An X-ray diffraction study shows that this complex consists of Co_3 and Co_2Fe triangles joined by a CC(O)OCHC group which can be described as an ester of a vinylidene group. The vinylidene part of the ligand is bonded to the Co_2Fe triangle. This compound crystallizes in the monoclinic space group C_{2h}^5—$P2_1/n$ with cell dimensions a = 8.645 (2) Å, b = 12.990 (2) Å, c = 26.883 (2) Å, β = 93.32 (2)°, and Z = 4. The structure was solved and refined to R and R_w values of 0.034 and 0.032, respectively, by using 5299 reflections. Other products isolated in this reaction are $Co_3(CO)_9(\mu_3\text{-}CH)$ (4% yield), $Co_3(CO)_9(\mu_3\text{-}CCH_3)$ (1% yield), $Fe_3(CO)_{12}$ (8% yield), $HFeCo_2(CO)_9(\mu_3\text{-}CH)$ (traces), $Fe_2Co(CO)_{10}(CCH_3)$ (traces), $[Co_3(CO)_9C]_2CO$ (4% yield), and $[Co_3(CO)_9C]_2$ (4% yield).

Introduction

Anionic ketenylidene clusters have been shown to be suitable precursors for the synthesis of mixed-metal carbide clusters,[1-4] illustrating the diverse chemistry of the ketenylidene ligand.

We thought that another possible route to mixed-metal carbide clusters would be to start with a cationic cluster containing a ketenylidene ligand such as $[Co_3(CO)_9CCO][PF_6]$ and to react it with anionic mononuclear complexes. To avoid electron-transfer reactions, in a first approach we have chosen a relatively weak nucleophilic anion, $[PPh_4][HFe(CO)_4]$. The reaction was very complex and did not give evidence of the formation of a mixed-metal carbide cluster. Nevertheless, the main product of the reaction was an unexpected compound resulting from the coupling of the starting $[Co_3(CO)_9CCO]^+$ with the in situ generated $[Co_2Fe(CO)_9CCHO]^-$ species, coupling occurring between the electrophilic carbon of the acylium group and the oxygen of the aldehyde ligand. The true nature of this compound was established by an X-ray structure determination.

Results and Discussion

At room temperature, $[PPh_4][HFe(CO)_4]$ reacts readily with a suspension of $[Co_3(CO)_9CCO][PF_6]$ in anhydrous dichloromethane, leading to a complex mixture which was separated by column chromatography. Successive elution with hexane, toluene, and diethyl ether allowed separation of the different products. Most of these were known and were identified by comparison of their spectral properties with published data. These are $Co_3(CO)_9(\mu_3\text{-}CH)$[5] (4% yield), $Co_3(CO)_9(\mu_3\text{-}CCH_3)$[6] (1% yield), $Fe_3(CO)_{12}$ (8% yield), $HFeCo_2(CO)_9(\mu_3\text{-}CH)$[7] (traces), $[Co_3(CO)_9C]_2CO$[6] (4% yield), and $Fe_2Co(CO)_{10}(CCH_3)$[9] (traces).

The main product of the reaction (20% yield) was a brown compound, slightly soluble in hexane, whose infrared spectrum in the ν(CO) stretching region is very complex but gives only evidence of terminal carbonyl groups. A peculiar feature of this spectrum was the occurrence of two weak bands at 2115 and 2102 cm^{-1}, suggesting the presence of two independent metallic groups. The proton NMR spectrum was not very informative, only one resonance being detected at 8.08 ppm, and the lack of solubility of the compound prevented application of ^{13}C NMR spectra.

Mass spectral analysis failed, due to the low volatility of the compound, and the only information came first from microanalysis which showed that this compound contained cobalt and iron in the approximate ratio 5/1. So the need for an X-ray structure determination for this compound was obvious.

The resulting structure is shown in Figure 1. Principal bond lengths and bond angles are gathered in Table I. The structure confirms what was suggested by the infrared data: the compound consists of two trimetallic units linked by an organic fragment. These two units are formed by three cobalt atoms and by two cobalt and one iron atoms, respectively. Each metallic center is bonded to three terminal carbonyl groups. The Co_3 triangle presents the conventional structural characteristics of $Co_3(CO)_9(\mu_3\text{-}CR)$ clusters[10] while the Fe–Co distances for the Co_2Fe triangle are in the range found for mixed FeCo clusters.[11] The organic fragment that links the two metallic triangles, C—C(O)—OC(H)=C, can be described as an ester of a vinylidene group. The vinylidene part is bonded to the $FeCo_2$ triangle: σ-bonded to Co(1) and Co(2) and π-bonded to Fe. The Co(1)–C(21) bond is shorter than the Co(2)–C(21), and the Fe–C(20) bond is longer than Fe–C(21) but is in the normal range for an Fe–C π-bond.[12] This dissymmetry of the π-bond seems a common feature for

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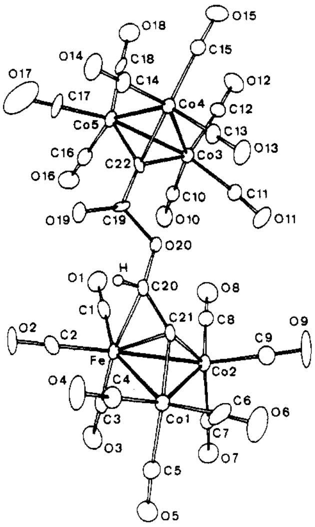

Figure 1. ORTEP view of $Co_3(CO)_9(CC(O)OCHC)Co_2Fe(CO)_9$ showing the atomic numbering scheme.

μ_3-η^2-bonded vinylidene ligands.[13] Distances and angles for the carboxylate group have normal values, but the C(19)–C(22) distance is shorter than a single carbon–carbon bond distance. A same phenomenon has been observed in $Co_3(CO)_9(\mu_3\text{-}C(O)R)$ complexes, and this has been attributed to the fact that the apical carbon retains a high character of sp hybridization.[10]

This complex can be considered as the result of the reaction of the starting cationic cluster $[Co_3(CO)_9CCO]^+$ with an anionic compound, $[FeCo_2(CO)_9(\mu_3\text{-}CCHO)]^-$, formed in situ. The condensation of two organic fragments results from the nucleophilic attack of the aldehydic oxygen onto the carbon of the acylium group. Nucleophilic attack on this carbon is a common feature of the reactivity of $[Co_3(CO)_9CCO]^+$ with nucleophiles,[14] and here it is certainly facilitated by the anionic character of the intermediate mixed iron cobalt cluster.

The subsequent equations summarize the proposed mechanism:

$$[Co_3(CO)_9CCO]^+ + [HFe(CO)_4]^- \rightarrow Co_3(CO)_9(\mu_3\text{-CHO}) + \text{“}Fe(CO)_4\text{”} \quad (1)$$

$$[Co_3(CO)_9(\mu_3\text{-CCHO})] + [HFe(CO)_4]^- \rightarrow [Co_2Fe(CO)_9(\mu_3\text{-CCHO})]^- + HCo(CO)_4 \quad (2)$$

$$[Co_3(CO)_9CCO]^+ + [Co_2Fe(CO)_9(\mu_3\text{-CCHO})]^- \rightarrow Co_5Fe(CO)_{18}(CC(O)OCHC) \quad (3)$$

($Fe_3(CO)_{12}$ would result from reaction 1.)

The byproducts isolated also gave evidence of the complexity of the reaction as transformation of the CCO unit into CCH_3 and CH ligands is also observed. Moreover, electron-transfer reactions are suggested by the formation of $[Co_3(CO)_9C]_2$ or $[Co_3(CO)_9C]_2CO$ compounds.[15]

Experimental Section

All reactions were performed under nitrogen by using standard Schlenk tube techniques. Infrared spectra were recorded with a Perkin-Elmer 225 spectrometer using hexane solutions. ^1H NMR spectra were recorded with a Bruker WH90 spectrometer.

Table I. Selected Bond Lengths (Å) and Angles (deg) with Estimated Standard Deviations in Parentheses

Bond Lengths			
Fe–Co(1)	2.5306 (10)	Co(3)–Co(4)	2.4713 (8)
Fe–Co(2)	2.5498 (9)	Co(3)–Co(5)	2.4625 (9)
Co(1)–Co(2)	2.4905 (10)	Co(4)–Co(5)	2.4810 (9)
Fe–C(1)	1.751 (6)	C(1)–O(1)	1.166 (8)
Fe–C(2)	1.820 (6)	C(2)–O(2)	1.109 (7)
Fe–C(3)	1.763 (5)	C(3)–O(3)	1.141 (7)
Co(1)–C(4)	1.763 (5)	C(4)–O(4)	1.136 (6)
Co(1)–C(5)	1.800 (6)	C(5)–O(5)	1.128 (7)
Co(1)–C(6)	1.823 (7)	C(6)–O(6)	1.117 (8)
Co(2)–C(7)	1.852 (5)	C(7)–O(7)	1.118 (7)
Co(2)–C(8)	1.782 (6)	C(8)–O(8)	1.133 (8)
Co(2)–C(9)	1.812 (6)	C(9)–O(9)	1.114 (7)
Co(3)–C(10)	1.799 (5)	C(10)–O(10)	1.141 (6)
Co(3)–C(11)	1.823 (5)	C(11)–O(11)	1.097 (7)
Co(3)–C(12)	1.839 (6)	C(12)–O(12)	1.102 (7)
Co(4)–C(13)	1.797 (5)	C(13)–O(13)	1.126 (7)
Co(4)–C(14)	1.811 (5)	C(14)–O(14)	1.125 (7)
Co(4)–C(15)	1.817 (5)	C(15)–O(15)	1.125 (7)
Co(5)–C(16)	1.798 (7)	C(16)–O(16)	1.108 (8)
Co(5)–C(17)	1.794 (6)	C(17)–O(17)	1.117 (9)
Co(5)–C(18)	1.786 (6)	C(18)–O(18)	1.170 (7)
C(19)–O(19)	1.228 (6)	C(21)–Fe	1.983 (4)
C(19)–O(20)	1.378 (5)	C(21)–Co(1)	1.856 (5)
C(19)–C(22)	1.410 (7)	C(21)–Co(2)	1.868 (4)
O(20)–C(20)	1.377 (6)	C(22)–Co(3)	1.911 (5)
C(20)–H	0.97 (1)	C(22)–Co(4)	1.899 (4)
C(20)–C(21)	1.362 (7)	C(22)–Co(5)	1.877 (5)
C(20)–Fe	2.221 (5)		
Bond Angles			
Co(1)–Fe–Co(2)	58.71 (3)	Co(4)–Co(3)–Co(5)	60.38 (2)
Fe–Co(1)–Co(2)	61.03 (3)	Co(3)–Co(4)–Co(5)	59.64 (3)
Fe–Co(2)–Co(1)	60.26 (3)	Co(3)–Co(5)–Co(4)	59.99 (2)
Fe–C(1)–O(1)	176.3 (5)	Co(3)–C(10)–O(10)	179.5 (4)
Fe–C(2)–O(2)	178.2 (5)	Co(3)–C(11)–O(11)	175.6 (5)
Fe–C(3)–O(3)	178.2 (5)	Co(3)–C(12)–O(12)	177.0 (5)
Co(1)–C(4)–O(4)	178.1 (5)	Co(4)–C(13)–O(13)	179.4 (5)
Co(1)–C(5)–O(5)	176.8 (5)	Co(4)–C(14)–O(14)	179.1 (5)
Co(1)–C(6)–O(6)	175.8 (6)	Co(4)–C(15)–O(15)	176.5 (5)
Co(2)–C(7)–O(7)	177.5 (4)	Co(5)–C(16)–O(16)	176.7 (6)
Co(2)–C(8)–O(8)	178.5 (5)	Co(5)–C(17)–O(17)	176.5 (8)
Co(2)–C(9)–O(9)	176.5 (6)	Co(5)–C(18)–O(18)	177.4 (5)
O(19)–C(19)–O(20)	119.1 (4)	C(19)–O(20)–C(20)	118.8 (4)
O(19)–C(19)–C(22)	126.3 (4)	Fe–C(21)–Co(1)	82.4 (2)
O(20)–C(19)–C(22)	114.6 (4)	Fe–C(21)–Co(2)	82.9 (2)
O(20)–C(20)–H	112 (3)	Co(1)–C(21)–Co(2)	84.0 (2)
Fe–C(20)–H	107 (3)	Co(3)–C(22)–Co(4)	80.9 (2)
C(21)–C(20)–H	124 (3)	Co(3)–C(22)–Co(5)	81.1 (2)
O(20)–C(20)–C(21)	122.4 (4)	Co(4)–C(22)–Co(5)	82.2 (2)

$[Co_3(CO)_9CCO][PF_6]$[16] and $[PPh_4][HFe(CO)_4]$[17] have been prepared by published procedures.

Reaction of $[Co_3(CO)_9CCO][PF_6]$ with $[PPh_4][HFe(CO)_4]$. To $[Co_3(CO)_9CCO][PF_6]$ (0.5 g, 0.8 mmol) in suspension in anhydrous CH_2Cl_2 (15 mL) was added $[PPh_4][HFe(CO)_4]$ (0.46 g, 0.8 mmol) dissolved in anhydrous CH_2Cl_2 (15 mL). The mixture was stirred 0.5 h and evaporated to dryness. The residue was chromatographed on a Florisil column.

Elution with hexane gave the following successively.

(i) A mixture of $Co_3(CO)_9(\mu_3\text{-CH})$ and $Co_3(CO)_9(\mu_3\text{-CCH}_3)$ that were separated by fractional crystallization in hexane. $Co_3(CO)_9(\mu_3\text{-CH})$ (15 mg): mass spectrum, m/z 442 with successive loss of 9 CO; IR ν(CO) 2106 (m), 2055 (vs), 2040 (s), 2023 (m), 1982 (w) cm^{-1} (lit. values[6] 2106.3 (m), 2057 (vs), 2041.5 (s), 2025.2 (w) cm^{-1}); ^1H NMR δ 12.11 (lit. value[18] 12.08 ppm). $Co_3(CO)_9(\mu_3\text{-CCH}_3)$ (4 mg): mass spectrum m/z 456 with successive loss of 9 CO; $Co_3(CO)_9(\mu_3\text{-CCH}_3)$ (4 mg): mass spectrum, m/z 456 with

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Table II. Crystal Data and Data Collection Details

	Crystal Data
formula	$C_{22}Co_5FeHO_{20}$
fw	935.5
cryst system	monoclinic
space group	C_{2h}^5—$P2_1/n$
a, Å	8.645 (2)
b, Å	12.990 (2)
c, Å	26.883 (2)
β, deg	93.32 (2)
V, $Å^3$	3014 (2)
Z	4
F(000)	1816
D(calcd), g cm^{-3}	2.06
cryst Size, mm	0.350 between {100} and $\{\bar{1}00\}$; 0.050 between {010} and $\{0\bar{1}0\}$; 0.125 between {001} and $\{00\bar{1}\}$; 0.075 between {011} and $\{0\bar{1}\bar{1}\}$
μ(Mo Kα), cm^{-1}	32.4
	Data Collection
temp, °C	20
radiatn	Mo Kα (λ = 0.71073 Å) from graphite monochromator
θ(min–max), deg	2.0–25.0
scan mode	ω–2θ
scan range, deg	0.80 + 0.35 tan θ
scan speed, deg min-1	2.0
receiving aperture, mm	
height	3.0
width	1.80 + 1.20 tan θ
take off angle, deg	3.5
intensity stds	$51\bar{3}$, 272, $32\bar{1}$ monitored every hour
orientatn reflctns	511, 080, $06\overline{13}$ checked every 100 reflections
collected reflctns	5955 (h,k,$\pm l$)
independent reflctns	5677 ($0kl$ and $0k\bar{l}$ merged; r_{av} = 0.035)

successive loss of 9 CO; IR ν(CO) 2102 (m), 2050 (vs), 2036 (s), 2017 (m) cm^{-1} (lit. values[6] 2102 (m), 2052 (vs), 2038 (s), 2018 (w) cm^{-1}); ^1H NMR δ 3.67 (lit. value[6] 3.69 ppm).

(ii) A mixture of $Fe_3(CO)_{12}$ (10 mg) and $HFeCo_2(CO)_9(\mu_3\text{-CH})$ (traces) that were separated by fractional crystallization. $HFeCo_2(CO)_9(\mu_3\text{-CH})$; mass spectrum, *m/z* 440 with successive loss of 9 CO; IR ν(CO) 2102 (m), 2055 (m), 2048 (s), 2036 (s), 2014 (m), 1990 (m) cm^{-1} (lit. value[7] 2101 (m), 2054 (s), 2047 (vs), 2038 (s), 2017 (m), 1988 (m), 1985 (m) cm^{-1}).

(iii) A mixture of $[Co_2(CO)_9C]_2CO$ (15 mg) and $Fe_2Co(CO)_{10}(\mu_3\text{-CCH}_3)$ (traces) that were separated by crystallization in hexane. $[Co_2(CO)_9C]_2CO$: mass spectrum, *m/z* 910 with successive loss of 19 CO; IR ν(CO) 2082 (s), 2061 (vs), 2030 (s), 1980 (w) cm^{-1} (lit. values[5] 2089.9 (s), 2064.7 (vs), 2036.6 (s), 1983 (vw) cm^{-1}). Anal. Calcd for $C_{21}O_{19}Co_6$: C, 27.69; Co, 38.90. Found: C, 27.33; Co, 38.22. $Fe_2Co(CO)_{10}(\mu_3\text{-CCH}_3)$: IR ν(CO) 2098 (w), 2049 (s), 2031 (s), 2008 (m), 1843 (w) cm^{-1} (lit. values[9] 2098 (w), 2047 (s), 2030 (s), 2008 (m), 1840 (w) cm^{-1}).

(iv) $[Co_3(CO)_9C]_2$ (15 mg): mass spectrum, *m/z* 882 with successive loss of 18 CO; IR ν(CO) 2082 (s), 2074 (vs), 2038 (vs), 2030 (m), 2020 (w), 2010 (w), 1980 (w) cm^{-1}. Anal. Calcd for $C_{20}O_{18}Co_6$: C, 27.21; Co, 40.13. Found: C, 27.30; Co, 39.8.

(v) $Co_5Fe(CO)_{18}C_4O_2H$ (75 mg) as brown crystals by crystallization in CH_2Cl_2/hexane: IR ν(CO) 2115 (w), 2102 (w), 2071 (vs), 2057 (m), 2050 (s), 2040 (s), 2025 (w), 2018 (w), 1990 (w) cm^{-1}. Anal. Calcd for $C_{22}HO_{20}Co_5Fe$: C, 28.20; H, 0.11; Co, 31.51; Fe, 5.98. Found: C, 28.29; H, 0.43; Co, 28.78; Fe, 5.19.

X-ray Structure Analysis. Collection and Reduction of X-ray Data. Crystals belong to the monoclinic system, space group $P2_1/n$. The selected crystal was sealed on a glass fiber and mounted on an Enraf-Nonius CAD4 diffractometer. Cell constants were obtained from the least-squares fit of the setting angles of 25 reflections in the range 12–14°, but one at 7.8°. A summary of crystal and intensity collection data is given in Table II. A total of 5955 reflections (hkl and $hk\bar{l}$) were recorded at a 2θ(Mo) maximum of 50° by procedures described elsewhere.[19] Data reduction was then performed.[20] Intensity standards, monitored every hour, showed a slight linear decay of 3%, from which data were corrected. Systematic absences were rejected ($h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$). The 5677 remaining reflections were corrected for absorption[21] (μ = 32.4 cm^{-1}; calculated transmission range 0.64–0.81). Equivalent reflections ($0kl$ and $0k\bar{l}$) were merged (R_{av} = 0.035).

Table III. Fractional Atomic Coordinates with Estimated Standard Deviations in Parentheses

atom	*x/a*	*y/b*	*z/c*
Fe	0.63929 (7)	0.60969 (5)	0.23771 (3)
Co(1)	0.61340 (7)	0.74763 (5)	0.17128 (3)
Co(2)	0.39218 (7)	0.71583 (5)	0.22463 (3)
Co(3)	0.49488 (7)	0.74626 (5)	0.44147 (3)
Co(4)	0.72552 (6)	0.85794 (5)	0.45323 (2)
Co(5)	0.74069 (8)	0.67313 (5)	0.47629 (3)
C(1)	0.6057 (6)	0.5438 (4)	0.2929 (2)
O(1)	0.5892 (4)	0.5034 (3)	0.3309 (2)
C(2)	0.8427 (6)	0.5735 (4)	0.2383 (2)
O(2)	0.9661 (4)	0.5497 (4)	0.2395 (2)
C(3)	0.5719 (6)	0.5101 (4)	0.1975 (2)
O(3)	0.5313 (5)	0.4463 (3)	0.1707 (2)
C(4)	0.8157 (6)	0.7569 (5)	0.1670 (2)
O(4)	0.9465 (5)	0.7611 (4)	0.1654 (2)
C(5)	0.5595 (7)	0.6723 (4)	0.1168 (2)
O(5)	0.5200 (5)	0.6280 (4)	0.0823 (2)
C(6)	0.5572 (6)	0.8759 (5)	0.1494 (2)
O(6)	0.5182 (6)	0.9517 (4)	0.1336 (2)
C(7)	0.2718 (5)	0.6383 (4)	0.1794 (2)
O(7)	0.2037 (5)	0.5892 (3)	0.1519 (2)
C(8)	0.3198 (6)	0.6717 (4)	0.2816 (2)
O(8)	0.2707 (5)	0.6446 (4)	0.3175 (2)
C(9)	0.2930 (5)	0.8388 (5)	0.2223 (2)
O(9)	0.2275 (5)	0.9127 (3)	0.2228 (3)
C(10)	0.4027 (6)	0.6248 (4)	0.4271 (2)
O(10)	0.3433 (5)	0.5482 (3)	0.4179 (2)
C(11)	0.3865 (5)	0.8214 (4)	0.3940 (2)
O(11)	0.3250 (5)	0.8628 (4)	0.3633 (2)
C(12)	0.3982 (6)	0.7825 (4)	0.4981 (2)
O(12)	0.3457 (5)	0.8029 (4)	0.5332 (2)
C(13)	0.6704 (6)	0.9541 (4)	0.4075 (2)
O(13)	0.6370 (5)	1.0141 (3)	0.3787 (2)
C(14)	0.9326 (6)	0.8784 (4)	0.4528 (2)
O(14)	1.0616 (5)	0.8902 (3)	0.4530 (2)
C(15)	0.6812 (6)	0.9210 (4)	0.5110 (2)
O(15)	0.6463 (5)	0.9586 (3)	0.5464 (2)
C(16)	0.6979 (6)	0.5406 (5)	0.4621 (2)
O(16)	0.6760 (6)	0.4592 (4)	0.4515 (2)
C(17)	0.9464 (6)	0.6582 (5)	0.4739 (3)
O(17)	1.0736 (7)	0.644 (1)	0.4730 (3)
C(18)	0.7124 (5)	0.6842 (4)	0.5414 (2)
O(18)	0.6906 (5)	0.6948 (4)	0.5836 (2)
C(19)	0.7485 (5)	0.7224 (4)	0.3666 (2)
O(19)	0.8741 (4)	0.6856 (3)	0.3568 (2)
O(20)	0.6477 (3)	0.7545 (3)	0.3281 (1)
C(20)	0.6962 (6)	0.7526 (4)	0.2802 (2)
H	0.807 (1)	0.763 (4)	0.279 (2)
C(21)	0.5955 (5)	0.7595 (3)	0.2395 (2)
C(22)	0.6941 (5)	0.7366 (3)	0.4145 (2)

Structure Solution and Refinement. The structure was solved by direct methods with SHELXS-86 program[22] using 5299 independent reflections. The six metal atoms were found. The full-matrix least-squares refinement and difference Fourier processus were achieved with SHELX-76 program[23] with 3250 reflections having $F_o^2 \geq 3\sigma(F_o^2)$. All atoms, but the hydrogen one, were refined with anisotropic thermal parameters.

The atomic scattering factors used were those proposed by Cromer and Waber[24] with anomalous dispersion effects.[25]

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Scattering factors for the hydrogen atom were taken from Stewart et.[26]

The final full-matrix least-squares refinement converged to $R = \sum||F_o| - F_c|| / \sum|F_o| = 0.034$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w(|F_o|^2]^{1/2} = 0.032$ with $w = 1/\sigma^2(F_o)$. The error in an observation of unit weight was $S = [\sum w(|F_o| - |F_c|)^2/(n - m)]^{1/2} = 1.9$ with $n = 3250$ observations and $m = 437$ variables. An analysis of variance showed no unusual trends. In the last cycle of refinement the shifts for all parameters were less than 0.76 (mean value 0.2σ). A final difference Fourier map showed a residual electron density of 0.7 e/Å^3 near metal atoms. The final fractional atomic coordinates are listed in Table III.

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Registry No. $Co_3(CO)_9[CC(O)OCHC]Co_2Fe(CO)_9]$, 113892-47-0; $[Co_3(CO)_9CCO][PF_6]$, 36834-91-0; $(PPh_4)[HFe(CO)_4]$, 103616-27-9; Fe, 7439-89-6; Co, 7440-48-4.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, and bond lengths and angles (4 pages); a listing of structure factors (16 pages). Ordering information is given on any current masthead page.

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Tetrahedral Complexes of Nickel(0) and Platinum(0) Containing a Chelating Olefinic Tertiary Phosphine. Synthesis, Reactivity, and X-ray Crystal Structures of $M(o\text{-}CH_2{=}CHC_6H_4PPh_2)_2$ (M = Ni, Pt)

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Zerovalent metal complexes of general formula $M(SP)_2$ [M = Ni (1), Pt (2)] containing (2-vinylphenyl)diphenylphosphine (*o*-styryldiphenylphosphine, $o\text{-}CH_2{=}CHC_6H_4PPh_2$, abbreviated SP) have been prepared by reaction of SP with the bis(1,5-cyclooctadiene)metal complexes, $M(1,5\text{-}COD)_2$. The nickel complex 1 has also been made by reduction of anhydrous bis(2,4-pentanedionato)nickel(II) with triethylaluminum in the presence of SP. Spectroscopic studies [NMR (^1H, ^{13}C, ^{31}P) and IR] suggest that the phosphorus atoms and both vinyl groups are coordinated, both in solution and in the solid state. Crystals of 1 are monoclinic, space group $P2_1/n$, with $a = 13.432$ (2) Å, $b = 11.486$ (2) Å, $c = 21.630$ (3) Å, $\beta = 104.34$ (1)°, and $Z = 4$; those of $2\cdot0.5C_6H_5CH_3$ are triclinic, space group $P\bar{1}$, with $a = 11.245$ (7) Å, $b = 14.127$ (4) Å, $c = 14.417$ (2) Å, $\alpha = 119.05$ (2)°, $\beta = 110.62$ (1)°, $\gamma = 91.05$ (1)°, and $Z = 2$. The structures were solved by direct (1) and heavy-atom methods (2) and refined by least-squares methods to $R = 0.041$ and $R_w = 0.045$ for 3299 independent reflections (1) and to $R = 0.026$ and $R_w = 0.030$ for 5273 independent reflections (2). In both molecules the metal atom is coordinated in a distorted tetrahedron by two bidentate SP ligands, the average M–P distances being 2.199 Å (1) and 2.284 Å (2). In 1 one vinyl group is coordinated symmetrically [Ni–C(19) = 2.033 (4) Å, Ni–C(20) = 2.037 (5) Å] while the other is bound asymmetrically, the Ni–C_α bond length [Ni–C(39) = 2.059 (4) Å] being significantly longer than the Ni–C_β separation [Ni–C(40) = 2.034 (5) Å]. By contrast, both vinyl groups in 2 are coordinated asymmetrically, although the difference in the Pt–C distances in each vinyl group is only just statistically significant and is such that Pt–C_α < Pt–C_β. The C═C distances show the expected lengthening on coordination [1.400 (6) Å (1); 1.416 (6) Å (2)]. The relative ordering of the metal–olefin bond strengths in 1 and 2 cannot be inferred unambiguously from the trends in various vinyl group parameters, such as ^1H and ^{13}C chemical shifts and coupling constants, C═C bond lengths, and bend-back angles of the vinylic hydrogen atoms. Free and coordinated SP exchange more readily in 2 than in 1. 2 reacts with HBF_4 or HPF_6 to give five-membered ring chelate (σ-alkyl)platinum(II) salts $[Pt(o\text{-}CH_3CHC_6H_4PPh_2)(SP)]Y$ ($Y = BF_4$, PF_6), as a mixture of cis and trans isomers **3a** and **3b**, respectively. An unstable nickel(II) analogue is formed similarly from 1.

Introduction

Nickel, palladium, and platinum in their zero oxidation states form a range of monomeric complexes with π-acceptor ligands such as CO, isocyanides, olefins, and tertiary phosphines and phosphites.[1-6] The metal atom in these complexes can adopt an 18e, 16e, or 14e configuration, and the stereochemical arrangement may be, respectively, tetrahedral (ML_4), trigonal planar (ML_3), or linear (ML_2). In general, small, terminally bound ligands such as CO and phosphites favor the formation of ML_4, whereas bulky tertiary phosphines and laterally bound ligands such as olefins and acetylenes favor ML_3 or ML_2. In addition,

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