

**3,4,4,5-Tetramethyl-4-silaheptane, 10:** colorless liquid;  $^1\text{H}$  NMR  $-0.12$  (s, 6 H (SiMe<sub>2</sub>)),  $0.6$ – $1.5$  ppm (broad envelope, 18 H (*sec*-Bu hydrogens));  $^{13}\text{C}$  NMR  $-6.57$  (q (Si(CH<sub>3</sub>))),  $13.59$  and  $13.85$  (q (*sec*-Bu methyls)),  $20.03$  (d (*sec*-Bu methine)),  $25.04$  ppm (t (*sec*-Bu methylene)); MS, *m/e* (relative intensity)  $172$  (3),  $157$  (2),  $115$  (50),  $101$  (4),  $87$  (8),  $73$  (100),  $59$  (72). Anal. Calcd for C<sub>10</sub>H<sub>24</sub>Si: C, 69.67; H, 14.03. Found: C, 69.83; H, 14.26.

**3,4,4,7-Tetramethyl-4-sila-5-nonene, 11:** MS, *m/e* (relative intensity)  $183$  (2, P – Me),  $141$  (100),  $127$  (8),  $113$  (20),  $99$  (31),  $85$  (43),  $73$  (40),  $59$  (52).

**3,4,4,7-Tetramethyl-4-silanonane, 12:** colorless liquid;  $^1\text{H}$  NMR  $0.1$  (s, 6 H),  $0.7$ – $2.6$  ppm (br, 22 H);  $^{13}\text{C}$  NMR  $-4.94$  (q (SiCH<sub>3</sub>)),  $10.86$ ,  $11.44$ ,  $13.52$ ,  $13.72$ ,  $18.56$ ,  $21.00$ ,  $24.90$ ,  $30.63$ ,  $37.59$  ppm; MS, *m/e* (relative intensity)  $185$  (2, P – Me),  $143$  (62),  $129$  (8),  $115$  (10),  $99$  (12),  $87$  (35),  $73$  (88),  $59$  (100). Anal. Calcd for C<sub>12</sub>H<sub>28</sub>Si: C, 71.90; H, 14.08. Found: C, 71.73; H, 14.09.

**5-(Dimethylfluorosilyl)-3,4,4,7-tetramethyl-4-silanonane, 13:** colorless oil;  $^1\text{H}$  NMR  $0.08$  (s, 6 H),  $0.25$  (d, 6 H,  $J(\text{H-F}) = 13$  Hz),  $0.6$ – $2.7$  ppm (br, 21 H);  $^{13}\text{C}$  NMR  $-4.75$  and  $-4.29$  (diastereotopic Si(CH<sub>3</sub>)<sub>2</sub>),  $-0.52$  (d,  $J(\text{C-F}) = 17.6$  Hz) and  $0.81$  (d,  $J(\text{C-F}) = 16.1$  Hz (diastereotopic SiF(CH<sub>3</sub>)<sub>2</sub>)),  $10.66$ ,  $11.15$ ,  $13.26$ ,  $18.40$ ,  $19.25$ ,  $20.54$ ,  $20.68$ ,  $24.64$ ,  $28.48$ ,  $30.24$ ,  $31.99$ ,  $36.48$  ppm; MS, *m/e* (relative intensity)  $261$  (2, P – Me),  $219$  (35),  $205$  (5),  $141$  (100),  $127$  (15),  $113$  (14),  $99$  (22),  $85$  (36),  $77$  (12),  $73$  (42),  $59$  (46). Anal. Calcd for C<sub>14</sub>H<sub>30</sub>Si<sub>2</sub>F: C, 60.80; H, 12.03. Found: C, 60.92; H, 12.09.

**2,4-Bis(2-methylbutyl)-1,1,3,3-tetramethyl-1,3-disilacyclobutane, 14:** colorless liquid;  $^1\text{H}$  NMR  $0.15$  (br, 12 H),  $0.76$ – $2.6$  ppm (br, 24 H);  $^{13}\text{C}$  NMR mixture of 68% *cis*-14 and 32% *trans*-14 estimated from spectrum,  $-5.14$  and  $2.79$  (q (Si-CH<sub>3</sub> is *cis* isomer)),  $-0.98$  (q (SiCH<sub>3</sub> in *trans* isomer)),  $11.44$  (CH<sub>3</sub>CH<sub>2</sub> of *sec*-Bu),  $14.76$  (d (ring C in *trans* isomer)),  $15.41$  (d (ring C in *cis* isomer)),  $18.99$  (t (CH<sub>3</sub> of *sec*-Bu)),  $29.26$  (t (methylene of *sec*-Bu)),  $32.12$  (t (methylene on ring in *cis* isomer)),  $32.84$  (t (methylene on ring in *trans* isomer)),  $37.98$  ppm (d, (methine of *sec*-Bu)); MS, *m/e* (relative intensity)  $284$  (4),  $269$  (1),  $227$  (30),  $157$  (42),  $141$  (80),  $131$  (90),  $113$  (16),  $99$  (28),  $85$  (100),  $73$  (85),  $59$  (88). Anal. Calcd for C<sub>18</sub>H<sub>36</sub>Si<sub>2</sub>: C, 67.52; H, 12.75. Found: C, 67.63; H, 12.82.

From the reactions with *n*-butyllithium the following compounds were isolated.

**3,3-Dimethyl-3-sila-1-heptene, 15:**  $^1\text{H}$  NMR  $-0.15$  (s, 6 H),  $0.2$ – $1.3$  (br, 9 H),  $5.0$ – $6.2$  ppm (m, 3 H);  $^{13}\text{C}$  NMR  $-3.97$  (q

(SiCH<sub>3</sub>)),  $13.13$ ,  $26.08$ , and  $25.75$  (t (CH<sub>2</sub>'s of *n*-Bu)),  $14.48$  (q (CH<sub>3</sub> of *n*-Bu)),  $130.51$  (d) and  $138.51$  ppm (t) (vinyl carbons); MS, *m/e* (relative intensity)  $142$  (1),  $127$  (6),  $114$  (8),  $99$  (4),  $85$  (100),  $71$  (38),  $59$  (70).

**5,5-Dimethyl-5-silanonane, 16:**  $^1\text{H}$  NMR  $-0.30$  (s, 6 H),  $0$ – $1.2$  ppm (br, 18 H);  $^{13}\text{C}$  NMR  $-3.77$  (q (SiCH<sub>3</sub>)),  $13.33$ ,  $26.40$ ,  $26.08$ , (t (CH<sub>2</sub>'s of *n*-Bu)),  $14.89$  ppm (q (CH<sub>3</sub> of *n*-Bu)); MS, *m/e* (relative intensity)  $172$  (1),  $157$  (6),  $115$  (78),  $101$  (12),  $73$  (74),  $59$  (100).

**5,5-Dimethyl-5-silaundecane, 17:**  $^1\text{H}$  NMR  $0.08$  (s, 6 H),  $0.6$ – $2.6$  ppm (br, 22 H);  $^{13}\text{C}$  NMR  $-3.84$  (q (SiCH<sub>3</sub>)),  $14.89$  (q (CH<sub>3</sub> of *n*-Bu)),  $13.66$  (CH<sub>3</sub> of *n*-hexyl),  $22.56$ ,  $23.86$ ,  $26.14$ ,  $26.46$ ,  $31.60$ ,  $32.90$ ,  $33.23$ ,  $33.49$  ppm (CH<sub>2</sub> groups); MS, *m/e* (relative intensity)  $185$  (4, P – Me),  $143$  (52),  $129$  (10),  $115$  (35),  $101$  (10),  $87$  (16),  $173$  (70),  $59$  (100).

**4-*n*-Pentyl-3,3,5,5-tetramethyl-3,5-disila-1-nonene, 18:** MS, *m/e* (relative intensity)  $231$  (6, P – Me),  $219$  (1),  $189$  (2),  $176$  (6),  $153$  (15),  $141$  (40),  $127$  (42),  $114$  (55),  $99$  (44),  $85$  (100),  $77$  (15),  $73$  (22),  $59$  (73).

**2,4-Di-*n*-pentyl-1,1,3,3-tetramethyl-1,3-disilacyclobutane, 19:** colorless liquid;  $^1\text{H}$  NMR  $0.15$  (s, 6 H),  $0.17$  (s, 6 H),  $0.6$ – $2.6$  ppm (br, 24 H);  $-3.71$  and  $-3.51$  (q (SiCH<sub>3</sub>)),  $13.66$  and  $14.63$  (q (CH<sub>3</sub> or *n*-Bu)),  $13.98$  and  $14.89$  (d (CH in ring)),  $22.63$ ,  $23.47$ ,  $24.40$ ,  $26.60$ ,  $28.22$ ,  $28.74$ ,  $29.07$ ,  $32.38$  ppm (t (CH<sub>2</sub> groups)); MS, *m/e* (relative intensity)  $227$  (18, P – Bu),  $213$  (3),  $199$  (2),  $171$  (4),  $153$  (18),  $141$  (48),  $131$  (88),  $115$  (14),  $99$  (12),  $85$  (55),  $73$  (52),  $59$  (100).

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**Registry No.** 1, X = F, 38755-76-9; 1, X = Cl, 1719-58-0; *cis*-4, 62518-77-8; *trans*-4, 62518-76-7; 5, 87656-63-1; 6, 87656-64-2; 9, 87656-65-3; 10, 87656-66-4; 11, 87681-17-2; 12, 87656-67-5; 13, 87656-68-6; *cis*-14, 87656-69-7; *trans*-14, 87656-72-2; 15, 24343-24-6; 16, 996-06-5; 17, 80054-50-8; 18, 87656-70-0; 19, 87656-71-1; 2-fluoro-2,5,5-trimethyl-3-(trimethylsilyl)-2-silahexane, 87681-18-3; *tert*-butyllithium, 594-19-4; *sec*-butyllithium, 598-30-1; *n*-butyllithium, 109-72-8; antimony trifluoride, 7783-56-4; antimony pentachloride, 7647-18-9; cyclopentadiene, 542-92-7; methoxytrimethylsilane, 1825-61-2; trimethylchlorosilane, 75-77-4; acetone, 67-64-1; methyl iodide, 74-88-4.

## Efficient Syntheses of New Fulvalene-Bridged Carbonyl Complexes of Cobalt, Ruthenium, Chromium, Molybdenum, and Tungsten

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A variety of new dimetallafulvalene carbonyl complexes have been prepared by slow addition of cold purified dihydrofulvalene in heptane to boiling solutions of metal carbonyls. Reaction of Co<sub>2</sub>(CO)<sub>8</sub> with dihydrofulvalene allows efficient preparation of (η<sup>5</sup>:η<sup>5</sup>-C<sub>10</sub>H<sub>8</sub>)(CO)<sub>4</sub>Co<sub>2</sub>. Ru<sub>3</sub>(CO)<sub>12</sub>, Cr(NCET)<sub>3</sub>(CO)<sub>3</sub>, Mo(CO)<sub>6</sub>, and W(NCET)<sub>3</sub>(CO)<sub>3</sub> react to form the intramolecularly metal-metal bonded complexes (η<sup>5</sup>:η<sup>5</sup>-C<sub>10</sub>H<sub>8</sub>)(CO)<sub>4</sub>Ru<sub>2</sub> and (η<sup>5</sup>:η<sup>5</sup>-C<sub>10</sub>H<sub>8</sub>)(CO)<sub>6</sub>M<sub>2</sub> (M = Cr, Mo, and W). Attempts to generate the analogous iron complexes were unsuccessful. Reaction of a mixture of Ru<sub>3</sub>(CO)<sub>12</sub> and Mo(CO)<sub>6</sub> with dihydrofulvalene affords a better than statistical yield of the mixed metal-metal bonded complex (η<sup>5</sup>:η<sup>5</sup>-C<sub>10</sub>H<sub>8</sub>)(CO)<sub>5</sub>MoRu.

### Introduction

Cyclopentadienylmetal carbonyl dimers and their derivatives are among the most extensively studied classes

of organometallic compounds. Dinuclear metal complexes are often postulated as simple models with which to study the interactions of molecules with metal surfaces.<sup>1</sup> Cy-

cllopentadienylmetal carbonyl dimers have been examined for catalytic and other reactivity and have been shown to undergo thermal or photochemical metal-metal bond homolysis resulting in fragmentation into mononuclear species.<sup>2,3</sup> A number of bridged dicyclopentadienyl ligands have been synthesized in order to facilitate the study of dinuclear interactions. Perhaps the most notable are the methylene-<sup>4</sup> and dimethylsilylene-<sup>5</sup> bridged complexes.

A simpler, yet relatively unexplored alternative would be the use of the bicyclopentadienyl (usually referred to as fulvalene) ligand as a means by which to strongly bind two metals in close enough vicinity to allow for metal-metal bond formation. The fulvalene ligand should allow for metal-metal bond cleavage without permitting fragmentation to mononuclear complexes. In the presence or absence of added ligands this system may promote metal-metal interaction without direct bonding and allow complexes to exhibit chemistry very different from that of analogous cyclopentadienyl compounds.<sup>6</sup> An additional, practical advantage of the presence of the fulvalene ligand is that routine <sup>1</sup>H NMR spectra of complexes become powerful tools for the structural analysis of derivatives. Instead of cyclopentadienyl singlets, the fixed nonequivalent fulvalene protons display characteristic patterns for each possible orientation of additional ligands. Furthermore, the potential complications arising from the presence of cis- and trans-cyclopentadienyl isomers is eliminated.

Previously reported preparations of fulvalene complexes have been the result of both planned and serendipitous syntheses. Examples of the latter include formation of the titanocene<sup>7</sup> and zirconocene<sup>8</sup> "dimers", the reactions of bisniobocene,<sup>9</sup> the reversible rearrangements of molybdenocene dimers,<sup>10</sup> and the oxidative coupling of mononuclear rhodium complexes.<sup>11</sup>

The first strategic approach to these compounds utilized Ullmann coupling reactions between halocyclopentadienylmetal moieties. A variety of structures including ( $\eta^5$ : $\eta^5$ -C<sub>10</sub>H<sub>8</sub>)( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Fe<sub>2</sub>,<sup>12</sup> ( $\eta^5$ : $\eta^5$ -C<sub>10</sub>H<sub>8</sub>)( $\eta^5$ -

C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Ru<sub>2</sub>,<sup>13</sup> ( $\eta^5$ : $\eta^5$ -C<sub>10</sub>H<sub>8</sub>)( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>FeRu,<sup>14</sup> ( $\eta^5$ : $\eta^5$ -C<sub>10</sub>H<sub>8</sub>)<sub>2</sub>Fe<sub>2</sub>,<sup>15</sup> ( $\eta^5$ : $\eta^5$ -C<sub>10</sub>H<sub>8</sub>)(CO)<sub>6</sub>Mn<sub>2</sub>,<sup>15b</sup> and ( $\eta^5$ : $\eta^5$ -C<sub>10</sub>H<sub>8</sub>)( $\eta^4$ -C<sub>4</sub>(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>)<sub>2</sub>Co<sub>2</sub><sup>16</sup> were prepared in modest yields. However, the generality of this method is severely limited by the availability of suitable starting materials.

Much greater success has been achieved with a scheme based on the preparation and reactions of fulvalene dianion.<sup>17-20</sup> Smart and co-workers have employed this method to prepare a great number of bis(fulvalene)dimetal sandwich complexes,<sup>20</sup> as well as the first cyclopentadienylmetal carbonyl dimer analogue ( $\eta^5$ : $\eta^5$ -C<sub>10</sub>H<sub>8</sub>)(CO)<sub>6</sub>Mo<sub>2</sub>, 4.

We now report<sup>6</sup> a related yet previously unexplored route to a variety of novel dimetallafulvalene carbonyls that exploits the previously unrecognized relative stability of dihydrofulvalene. The method has opened up a new area of research into potential binuclear catalysts based on this ligand.

## Results and Discussion

Our initial attempts to prepare new dimetallafulvalene carbonyl complexes by reaction of fulvalene dianion with metal carbonyls or metal carbonyl halides resulted in discouragingly low yields. Instead we began to explore the possibility of treating dihydrofulvalene directly with metal carbonyls, in analogy to the established routes to cyclopentadienylmetal carbonyls from cyclopentadiene. Dihydrofulvalene is prepared by treating sodium cyclopentadienide with 0.5 equiv of iodine in THF. Attempts to isolate the product have reportedly resulted in polymerization to an intractable solid.<sup>17</sup>

In our first experiments, freshly prepared solutions of dihydrofulvalene in THF (also containing NaI and minor impurities) were kept cold (-78 °C) during slow addition to boiling solutions of metal carbonyls. This procedure led to low yields of the desired products and large amounts of insoluble precipitates. Yields dramatically increased when a rapid low-temperature H<sub>2</sub>O-THF/hydrocarbon extraction procedure was used to remove the dihydrofulvalene from the impurities generated in its formation (see Experimental Section). Reaction of the purified solution resulted in efficient syntheses of complexes 1-5 and a better than statistical entry into the mixed-metal system 6, the first of its kind.

Complexes 1, 2, and 4 were prepared by reaction with the commercially available Co<sub>2</sub>(CO)<sub>8</sub>, Ru<sub>3</sub>(CO)<sub>12</sub>, and Mo(CO)<sub>6</sub>. Efficient syntheses of complexes 3 and 5 required the preparation of the readily accessible propionitrile complexes Cr(NCET)<sub>3</sub>(CO)<sub>3</sub> and W(NCET)<sub>3</sub>(CO)<sub>3</sub>.<sup>21</sup> The corresponding chromium and tungsten hexacarbonyls are insufficiently labile and the tris(acetonitrile) complexes

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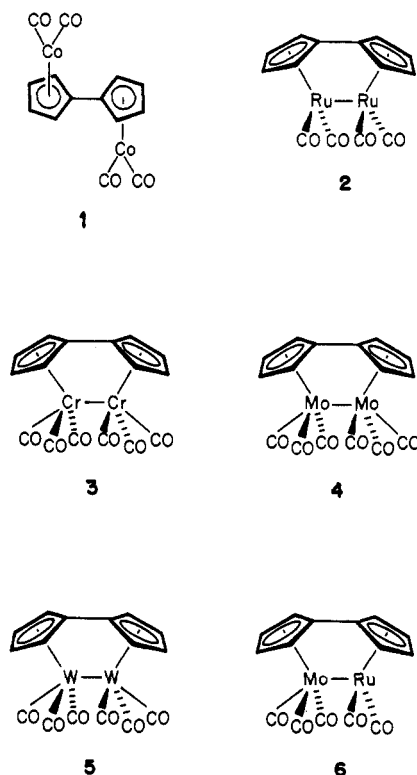
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to insoluble to react with dihydrofulvalene before it polymerizes. Attempts to prepare the iron complex analogous to 2 have been unsuccessful. Perhaps a shorter Fe-Fe bond may require too great a distortion of the fulvalene ligand to allow stable intramolecular metal-metal bonding. The X-ray structure of 2 reveals a major distortion of the fulvalene ligand to enable the formation of a Ru-Ru bond (2.821 Å).<sup>6</sup>

The successful synthesis of the homodinuclear complexes 1-5 suggested that it might be possible to synthesize mixed-metal analogues. Reaction of dihydrofulvalene with a 1:1 (per equivalent metal) mixture of  $\text{Ru}_3(\text{CO})_{12}$  and  $\text{Mo}(\text{CO})_6$  resulted in a slightly better than statistical yield (58% of total fulvalene complexes) of complex 6. To test whether metal-metal exchange is possible after initial complex formation two crossover experiments were performed. In the first, a solution of 6 and, in the second, a mixture of 2 and 4 were both heated (120 °C, 6 h) and irradiated (Hanovia high-pressure mercury lamp, 1 h) without any detectable metal-metal exchange. Since mixtures of cyclopentadienylmetal dimers have been shown to rapidly scramble,<sup>2,3</sup> mixed-metal fulvalenes may prove superior for the study of mixed-metal interactions.

The initial products of the reaction of cyclopentadiene with ruthenium<sup>22</sup> and tungsten<sup>23</sup> carbonyls are the corresponding mononuclear cyclopentadienylmetal carbonyl hydrides. In contrast, the employment of dihydrofulvalene in our systems leads to the direct isolation of complexes 2 and 5 (and also 3, 4, and 6). Examination of the reaction mixtures after short reaction times or at lower reaction temperatures, and attempted hydrogenolysis of 2-6 all fail to generate detectable amounts of the suspected dihydride intermediates. The fulvalene ligand may promote rapid intramolecular  $\text{H}_2$  extrusion not accessible to mononuclear hydrides.

All our compounds were found to be more air stable than the analogous cyclopentadienyl complexes. Except for 1,

Table I. Electronic Absorption Maxima. Comparison between Metal-Metal Bonded Fulvalene Complexes and Analogous Cyclopentadienyl Metal Dimers<sup>a</sup>

complex	$\sigma \rightarrow \sigma^*$ , nm	other transitions (> 300 nm)
$(\eta^5\text{-}\eta^5\text{-C}_{10}\text{H}_8)(\text{CO})_4\text{Ru}_2$	332	400 (sh)
$[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{Ru}]_2$ <sup>24</sup>	330	435 (sh)
$(\eta^5\text{-}\eta^5\text{-C}_{10}\text{H}_8)(\text{CO})_6\text{Cr}_2$	450	370 (?)
$[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{Cr}]_2$ <sup>25</sup>	488	590 ( $d\pi \rightarrow \sigma^*$ )
$(\eta^5\text{-}\eta^5\text{-C}_{10}\text{H}_8)(\text{CO})_6\text{Mo}_2$	378	558 ( $d\pi \rightarrow \sigma^*$ )
$[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{Mo}]_2$ <sup>25</sup>	388	512 ( $d\pi \rightarrow \sigma^*$ )
$(\eta^5\text{-}\eta^5\text{-C}_{10}\text{H}_8)(\text{CO})_6\text{W}_2$	353	555 ( $d\pi \rightarrow \sigma^*$ )
$[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{W}]_2$ <sup>25</sup>	362	493 ( $d\pi \rightarrow \sigma^*$ )

<sup>a</sup> For comparative purposes, the absorption spectra of the fulvalene complexes were recorded in the same solvent as the Cp complexes (isooctane). Quantative measurements required the use of solvents in which fulvalene complexes are more soluble (see Experimental Section).

all are completely air stable as solids and oxidize only slowly (over a period of many hours) in solutions protected from light.

The electronic spectra of 2-5 and the analogous cyclopentadienylmetal carbonyl dimers are compared in Table I. The intense bands assigned to the metal-metal  $\sigma \rightarrow \sigma^*$  transition appear at higher energy for fulvalene complexes of the group 6B metals, while it is essentially the same for 2 and the non-carbonyl-bridged isomer of  $[\text{CpRu}(\text{CO})_2]_2$ .<sup>24</sup> The broad  $d\pi \rightarrow \sigma^*$  transitions of the molybdenum and tungsten derivatives are centered at significantly lower energy than the analogous bands in their cyclopentadienyl analogues.

The chemical shift differences between the  $\alpha$  and  $\beta$  protons in the  $^1\text{H}$  NMR spectra of fulvalene ligands appear to correlate with the presence of metal-metal bonding, as observed earlier<sup>17</sup> (see Experimental Section). Interestingly, the  $^1\text{H}$  NMR spectrum of hexacarbonyl(fulvalene)dichromium (3) exhibits sharp lines, in contrast to the analogous dimer  $[\text{CpCr}(\text{CO})_3]_2$ , which exists in equilibrium with its 17-electron monomer, resulting in severe NMR line broadening at room temperature.<sup>26</sup> Future work is aimed at establishing whether the fulvalene ligand in 3 acts to prevent the formation of paramagnetic species by inhibiting bond homolysis or whether it electronically couples two non metal-metal bonded paramagnetic halves to create a diamagnetic complex. This question as well as the unusual thermo- and photochemical<sup>6</sup> properties of all new complexes are currently under investigation.

## Experimental Section

**General Procedures.** All manipulations were carried out by using standard Schlenk techniques under nitrogen or in a Vacuum Atmospheres Inc. glovebox. THF and glyme were distilled from sodium benzophenone ketyl prior to use. Other solvents were distilled from the appropriate drying agents and degassed, except for chromatography solvents, which were simply deoxygenated with  $\text{N}_2$ .  $\text{Na}(\text{DME})\text{C}_5\text{H}_5$ <sup>17</sup> and  $\text{W}(\text{NCEt})_3(\text{CO})_3$ <sup>21</sup> were prepared by literature methods. All metal carbonyls were purchased from Strem Chemicals Inc. and used without further purification. Preparative high-pressure liquid chromatography was carried out on a Waters Prep LC/System 500A using two silica cartridges. Column chromatography was performed by using Alfa neutral

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alumina at activity II.  $^1\text{H}$  NMR spectra were recorded on U.C. Berkeley 200- and 250-MHz instruments equipped with Cryo-magnets Inc. magnets and Nicolet Model 1180 data collection systems. IR spectra were recorded on a Perkin-Elmer Model 681 spectrophotometer. Electronic spectra were recorded on a Hewlett-Packard Model 8450A UV-visible spectrophotometer. Mass spectral analysis was performed on an Atlas MS-12 instrument at 70 eV. Natural isotopic distributions produced broad peak envelopes; only the major peak is reported. Elemental analyses were carried out by the U.C. Berkeley College of Chemistry Microanalytical Laboratory.

**Preparation of Dihydrofulvalene Solution.** In an inert-atmosphere drybox, a 500-mL two-neck round-bottom flask was equipped with a magnetic stirrer bar and charged with Na-(DME) $\text{C}_5\text{H}_5$  (5.35 g, 30.0 mmol). The flask was sealed with rubber septa and removed from the box. Dry, oxygen-free THF (100 mL) was added via cannula and the resulting stirred solution cooled to  $-78^\circ\text{C}$ . Iodine (3.81 g, 15.0 mmol) in dry degassed THF (25 mL) was added by syringe. The flask was allowed to warm toward room temperature (with stirring) for exactly 25 min. Chilled ( $0^\circ\text{C}$ ) degassed heptane (150 mL) was added against  $\text{N}_2$  and the mixture stirred for 30 s. Subsequent to the addition of a chilled ( $0^\circ\text{C}$ ) aqueous 1%  $\text{Na}_2\text{S}_2\text{O}_3$  solution (150 mL) the solution was stirred vigorously for 1 min. The entire mixture was immediately transferred into an  $\text{N}_2$ -filled separatory funnel and the lower aqueous layer discarded. The upper layer was separated and shaken vigorously for 1 min in an  $\text{N}_2$ -filled flask containing anhydrous  $\text{Na}_2\text{SO}_4$  (50 g). The clear yellow dihydrofulvalene solution was decanted from the drying agent into an  $\text{N}_2$ -filled flask and immediately cooled to  $-78^\circ\text{C}$  with stirring. This was the standard dihydrofulvalene solution used to prepare compounds 1–6. *Note!* All manipulations following the 25-min warm-up period must be performed in less than 5 min to prevent significant ligand loss due to polymerization.

( $\eta^5\text{-}\eta^5\text{-C}_{10}\text{H}_8$ )(CO) $_4\text{Co}_2$  (1).  $\text{Co}_2(\text{CO})_8$  (3.42 g, 10.0 mmol) was placed in a 1000-mL round-bottom flask in the glovebox. The flask was equipped with a magnetic stirrer bar and a rubber septum capped reflux condenser and removed from the box. Dry, degassed  $\text{CH}_2\text{Cl}_2$  (400 mL) was added (via cannula), and the stirred solution was heated to reflux. The standard dihydrofulvalene solution (see above) was added via syringe in portions of 5 mL over a period of 4 h and the resulting solution heated to reflux for an additional 36 h. After the solution was cooled, the solvent was removed by vacuum transfer and the remainder left on the vacuum line overnight at 0.02 torr to remove residual  $\text{CpCo}(\text{CO})_2$ . The residue was taken up in  $\text{Et}_2\text{O}$  (25 mL) and chromatographed under  $\text{N}_2$  on alumina (250 g) eluting with pentane. Traces of  $\text{CpCo}(\text{CO})_2$  were eluted as a rapidly moving faint orange band. When the eluent was changed to  $\text{Et}_2\text{O}$ , a dark orange-red band was obtained. This fraction was concentrated to 15 mL, diluted to 40 mL with pentane, and cooled to  $-10^\circ\text{C}$  causing 1 (2.20 g) to crystallize. Evaporation of the remaining solution, dissolution in pentane, and crystallization yielded an additional crop (0.84 g) of 1. Recrystallization from  $\text{Et}_2\text{O}$ /pentane (1:4) resulted in analytically pure 1 (2.86 g, 80%) as dark red cubes: mp  $97\text{--}98^\circ\text{C}$ ;  $^1\text{H}$  NMR (250 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  4.69 (dd, 4 H,  $J = 2.5, 2.5$  Hz), 4.35 (dd, 4 H,  $J = 2.5, 2.5$  Hz); IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu_{\text{CO}}$  2024 (vs), 1965 (vs)  $\text{cm}^{-1}$ ; UV  $\lambda_{\text{max}}$  278 (sh,  $\epsilon$  20 000), 289 (30 000), 301 (51 000), 315 (59 000), 400 (sh, 5000) nm; MS,  $m/e$  (relative intensity) 358 ( $\text{M}^+$ , 0.32), 330 ( $\text{M}^+ - \text{CO}$ , 75.8), 302 ( $\text{M}^+ - 2\text{CO}$ , 59.5), ( $\text{M}^+ - 3\text{CO}$ , 84.5), 246 ( $\text{M}^+ - 4\text{CO}$ , 96.6), 59 (Co, 100). Anal. Calcd for  $\text{C}_{14}\text{H}_8\text{O}_4\text{Co}_2$ : C, 46.97; H, 2.25. Found: C, 47.15; H, 2.28.

( $\eta^5\text{-}\eta^5\text{-C}_{10}\text{H}_8$ )(CO) $_4\text{Ru}_2$  (2). A solution of  $\text{Ru}_3(\text{CO})_{12}$  (4.26 g, 6.67 mmol) in dry degassed glyme (400 mL) was heated to reflux under an  $\text{N}_2$  purge. The standard dihydrofulvalene solution was added via syringe in 5-mL aliquots over a period of 4 h and the mixture boiled for an additional 20 h.

After being cooled, the entire reaction mixture was filtered through a  $\text{CH}_2\text{Cl}_2$ -packed alumina column (250 g). The column was washed with  $\text{CH}_2\text{Cl}_2$  (250 mL) and the total eluent concentrated to about 40 mL causing crude 2 to separate as a bright yellow solid. The remaining solution was preadsorbed on alumina (25 g) and applied to a hexane-packed alumina column (300 g). The column was washed with hexane and compound 2 subsequently removed with  $\text{CH}_2\text{Cl}_2$  (yellow band). This material was combined with the crude product and crystallized twice from

$\text{CH}_2\text{Cl}_2$  to give bright yellow crystals of analytically pure 2 (3.45 g, 78%): mp  $288\text{--}290^\circ\text{C}$ ;  $^1\text{H}$  NMR (200 MHz, acetone- $d_6$ )  $\delta$  5.90 (dd, 4 H,  $J = 2.2, 2.1$  Hz), 4.40 (dd, 4 H,  $J = 2.1, 2.1$  Hz); IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu_{\text{CO}}$  2020 (vs), 1952 (vs)  $\text{cm}^{-1}$ ; UV  $\lambda_{\text{max}}$  (THF) 243 ( $\epsilon$  9700), 273 (11 000), 329 (7100), 388 (sh) (1500) nm; MS,  $m/e$  443 ( $\text{M}^+$ , 92.0), 432 ( $\text{M}^+ - \text{CO}$ , 1.6), 415 ( $\text{M}^+ - 2\text{CO}$ , 63.1), 387 ( $\text{M}^+ - 3\text{CO}$ , 85.8), 359 ( $\text{M}^+ - 4\text{CO}$ , 100). Anal. Calcd for  $\text{C}_{14}\text{H}_8\text{O}_4\text{Ru}_2$ : C, 38.03; H, 1.82. Found: C, 38.23; H, 1.97.

( $\eta^5\text{-}\eta^5\text{-C}_{10}\text{H}_8$ )(CO) $_6\text{Cr}_2$  (3). A solution of  $\text{Cr}(\text{CO})_6$  (4.40 g, 20.0 mmol) in dry degassed propionitrile (400 mL) was stirred and heated to reflux with an  $\text{N}_2$  purge for 24 h. The solvent was removed via vacuum transfer and the remaining yellow solid left under vacuum overnight. Purification of  $\text{Cr}(\text{NCEt})_3(\text{CO})_3$  is unnecessary and results in much lower yields based on  $\text{Cr}(\text{CO})_6$ . The flask was fitted with a septum-capped reflux condenser (under  $\text{N}_2$ ), and dry degassed glyme (400 mL) was added via cannula. The stirred mixture was brought to reflux causing all of the solid to dissolve. Without delay, the standard dihydrofulvalene solution was added via syringe in 5-mL portions over a period of 30 min and the reaction mixture boiled for an additional 20 h. After being cooled, the solution was filtered through a  $\text{CH}_2\text{Cl}_2$ -packed alumina (250 g) column under  $\text{N}_2$ . The column was washed with  $\text{CH}_2\text{Cl}_2$  (250 mL) and the total eluent concentrated to about 40 mL causing crude 3 to separate as a dark green solid. The remaining solution was treated as in the preparation of 2 and the combined crude product recrystallized twice from  $\text{CH}_2\text{Cl}_2$  (in the dark) to give dark green crystals of analytically pure 3 (1.68 g, 42%). *Note:* All operations, especially final purification, must be performed with minimum exposure to light as 3 is very photoreactive. Crystals darken above  $250^\circ\text{C}$  without melting:  $^1\text{H}$  NMR (250 MHz, acetone- $d_6$ )  $\delta$  5.25 (dd, 4 H,  $J = 2.2, 2.3$  Hz), 4.54 (dd, 4 H,  $J = 2.2, 2.2$  Hz); IR (KBr)  $\nu_{\text{CO}}$  2000 (s), 1920 (vs), 1900 (vs)  $\text{cm}^{-1}$ ; UV  $\lambda_{\text{max}}$  ( $\text{Et}_2\text{O}$ ) 250 (sh,  $\epsilon$  24 000), 370 (5400), 448 (20 000) nm; MS,  $m/e$  400 ( $\text{M}^+$ , 6.0), 344 ( $\text{M}^+ - 2\text{CO}$ , 6.9), 316 ( $\text{M}^+ - 3\text{CO}$ , 19.5), 288 ( $\text{M}^+ - 4\text{CO}$ , 8.3), 260 ( $\text{M}^+ - 5\text{CO}$ , 77.6), 232 ( $\text{M}^+ - 6\text{CO}$ , 100). Anal. Calcd for  $\text{C}_{16}\text{H}_8\text{O}_6\text{Cr}_2$ : C, 48.02; H, 2.01. Found: C, 48.13; H, 2.13.

( $\eta^5\text{-}\eta^5\text{-C}_{10}\text{H}_8$ )(CO) $_6\text{Mo}_2$  (4). A solution of  $\text{Mo}(\text{CO})_6$  (5.27 g, 20.0 mmol) in dry degassed glyme (400 mL) was heated to reflux under  $\text{N}_2$ . Without delay the standard dihydrofulvalene solution was added via syringe in 5-mL aliquots over a period of 4 h and the mixture boiled for an additional 20 h. Workup as in the preparation of 2 gave after two recrystallizations from  $\text{CH}_2\text{Cl}_2$  (in the dark under  $\text{N}_2$ ) purple crystals of pure 4 (2.93 g, 60%), mp  $279\text{--}280^\circ\text{C}$ . Physical and spectral properties match those reported in the previous preparation of 4.<sup>17</sup> This compound is also accessible in 88% yield by the procedure used in the preparation of 5.

( $\eta^5\text{-}\eta^5\text{-C}_{10}\text{H}_8$ )(CO) $_6\text{W}_2$  (5).  $\text{W}(\text{NCEt})_3(\text{CO})_3$  was prepared according to the method of Kubas<sup>21</sup> by heating  $\text{W}(\text{CO})_6$  in propionitrile. The complex (8.66 g, 20.0 mmol) in dry degassed glyme (400 mL) was then heated to reflux under  $\text{N}_2$ . Without delay the standard dihydrofulvalene solution was added via syringe in 5-mL aliquots over a period of 2 h and the mixture boiled for an additional 20 h. Workup as in the preparation of 2 gave dark purple crystals of analytically pure 5 (4.78 g, 72%): crystals darken above  $350^\circ\text{C}$  without melting;  $^1\text{H}$  NMR (200 MHz, acetone- $d_6$ )  $\delta$  5.83 (dd, 4 H,  $J = 2.2, 2.3$  Hz), 5.04 (dd, 4 H,  $J = 2.3, 2.2$  Hz); IR (KBr)  $\nu_{\text{CO}}$  2000 (s), 1940 (vs), 1880 (vs)  $\text{cm}^{-1}$ ; UV  $\lambda_{\text{max}}$  ( $\text{Et}_2\text{O}$ ) 278 (sh,  $\epsilon$  13 000), 353 (17 000), 548 (740) nm; MS,  $m/e$  664 ( $\text{M}^+$ , 14.4), 636 ( $\text{M}^+ - \text{CO}$ , 3.1), 608 ( $\text{M}^+ - 2\text{CO}$ , 11.2), 580 ( $\text{M}^+ - 3\text{CO}$ , 7.7), 552 ( $\text{M}^+ - 4\text{CO}$ , 99.5), 524 ( $\text{M}^+ - 5\text{CO}$ , 94.9), 494 ( $\text{M}^+ - 6\text{CO}$ , 53.4), 247 ( $\text{C}_6\text{H}_5\text{W}$ , 100). Anal. Calcd for  $\text{C}_{16}\text{H}_8\text{O}_6\text{W}_2$ : C, 28.95; H, 1.21. Found: C, 29.20; H, 1.16.

( $\eta^5\text{-}\eta^5\text{-C}_{10}\text{H}_8$ )(CO) $_5\text{MoRu}$  (6). A mixture of  $\text{Mo}(\text{CO})_6$  (2.64 g, 10.0 mmol) and  $\text{Ru}_3(\text{CO})_{12}$  (2.13 g, 3.33 mmol) in dry degassed glyme (400 mL) was heated to reflux under  $\text{N}_2$ . The standard dihydrofulvalene solution was added via syringe in 5-mL aliquots over a period of 2 h and the mixture heated to reflux for an additional 20 h. Workup as described in the synthesis of 2 gave a mixture (3.95 g) which was analyzed by NMR spectroscopy to contain 6 (58%), 4 (24%), and 2 (18%). Portions (0.5 g at a time) of the mixture were dissolved in THF (10 mL) and separated by preparative high-pressure liquid chromatography using two silica columns and 10% THF in hexane as the eluent. Compounds separated in the order 2 (yellow), 6 (orange), and 4 (purple) and were converted to analytical purity by crystallizing once from

$\text{CH}_2\text{Cl}_2$ . This gave 2 (0.39 g, 8.8%) and 4 (0.48 g, 6.8%), in addition to the desired 6. Complex 6 formed metallic orange crystals (1.95 g, 42%): mp 256–258 °C;  $^1\text{H}$  NMR (250 MHz, acetone- $d_6$ )  $\delta$  5.88 (dd, 2 H,  $J = 2.2, 2.1$  Hz), 5.53 (dd, 2 H,  $J = 2.3, 2.3$  Hz), 4.79 (dd, 2 H,  $J = 2.4, 2.3$  Hz), 4.42 (dd, 2 H,  $J = 2.2, 2.1$  Hz); IR (KBr)  $\nu_{\text{CO}}$  2020 (s), 1942 (s), 1935 (s), 1868 (s)  $\text{cm}^{-1}$ ; UV  $\lambda_{\text{max}}$  309 ( $\epsilon$  15000), 378 (9100), 470 (sh, 880) nm; MS,  $m/e$  465 ( $\text{M}^+$ , 19.6), 438, ( $\text{M}^+ - \text{CO}$ , 15.9), 411 ( $\text{M}^+ - 2\text{CO}$ , 7.0), 381 ( $\text{M}^+ - 3\text{CO}$ , 71.0), 352 ( $\text{M}^+ - 4\text{CO}$ , 16.2), 324 ( $\text{M}^+ - 5\text{CO}$ , 100). Anal. Calcd for  $\text{C}_{15}\text{H}_8\text{O}_5\text{MoRu}$ : C, 38.73; H, 1.73. Found: C, 38.70; H, 1.75.

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## Chemistry of $\text{Co}^+$ and $\text{Co}(\text{ligand})_n^+$ with Mono- and Bisubstituted $n$ -Butanes in the Gas Phase: Using a Simple "Ligand Competition" Model and Collision-Induced Dissociation Analysis To Provide Insights into Product Structures

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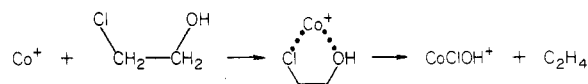
The gas-phase chemistry of ions of the type  $\text{Co}^+$ ,  $\text{Co}(\text{CO})_x^+$ , and  $\text{Co}(\text{CO})_x\text{NO}^+$  with mono- and bisubstituted  $n$ -butanes is discussed. Bifunctional molecules exhibit a much richer chemistry with these metal centers than do the monofunctional compounds. If  $\text{Co}^+$  must "choose" between two groups such as Br and OH, some preference for the halogen is indicated. In such mass spectrometric studies, the mass of a product ion is frequently insufficient for determining what type of reaction actually occurred. This text discusses a model that predicts the relative strengths of metal-ligand interactions. By postulating possible reaction intermediates and using the suggested model to determine which neutrals would be lost from each possible intermediate, information on product ion structures becomes available. Collision-induced dissociation experiments are also used as a probe of ionic product structures. These experiments also yield a lower limit on the  $\text{Co}^+$ -butadiene bond strength of 85.9 kcal/mol.

### Introduction

Investigations in the dynamics of bimolecular ion-molecule reactions under low-pressure conditions in the gas phase have been very productive. With use of ion cyclotron resonance spectrometry<sup>1</sup> and other mass spectrometric methods, the chemistry of metal- and metal-containing ions with organic molecules can be studied in the gas phase, yielding mechanistic, thermodynamic, and kinetic information on the basic processes and driving forces of organometallic chemistry.<sup>2</sup> Also, the specificity with which metal ions react with organic functional groups suggests that metal ion chemical ionization may be a useful mass spectrometric technique.<sup>3</sup>

Most of the work reported to date in this area involves the chemistry of transition-metal ionic species with organic compounds containing one functional group or no functional groups (alkanes). A major research effort in this laboratory is the study of the chemistry of ionic metal

centers with multifunctional compounds.<sup>3b</sup> For an evaluation of the eventual utility of metal ion chemical ionization, it must be determined how the products of the reaction between a metal ion and an organic compound containing more than one functional group are related to the reactant molecule. If  $\text{Co}^+$  reacts with a saturated hydrocarbon skeleton containing, e.g., a Cl and an OH group, one or more of the following may be observed: (1) Products representative of alcohol reactions and products typical of alkyl halide reactions are formed. (2) Products only typical of one functional group are formed (indicating the  $\text{Co}^+$  would show a preference for one functional group over another). (3) Products that are unique to this combination of functional groups are formed. Reactions exemplary of all three possibilities have been observed.<sup>3b</sup> In a previous report from our laboratory,<sup>3b</sup> bifunctional compounds with both groups in close proximity were studied. In this case, the interaction of both functional groups with the reactant metal ion is geometrically accessible and apparently occurs, e.g.



To determine whether  $\text{Co}^+$  would exhibit a preference for one functional group over another, the decision was made to investigate a series of 1,4-bisubstituted  $n$ -butanes. It was initially thought that the four-carbon chain would be

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