

# Synthesis of a Heptanuclear Rhenium–Iridium Carbido Carbonyl Cluster and of (Triphenylphosphine)gold(I) Derivatives

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The octanuclear cluster  $[\text{Re}_5\text{Ir}(\mu_6\text{-C})(\text{CO})_{17}(\mu_3\text{-Re}(\text{CO})_3)_2]^{2-}$  loses a  $[\text{Re}(\text{CO})_3]^+$  capping unit in refluxing acetonitrile to give the heptanuclear cluster  $[\text{Re}_5\text{Ir}(\mu_6\text{-C})(\text{CO})_{17}(\mu_3\text{-Re}(\text{CO})_3)]^{3-}$ . The latter compound can be capped with  $[\text{AuPPh}_3]^+$  groups to form the monogold and digold derivatives  $[\text{Re}_6\text{IrC}(\text{CO})_{20}(\text{AuPPh}_3)]^{2-}$  and  $[\text{Re}_6\text{IrC}(\text{CO})_{20}(\text{AuPPh}_3)_2]^-$ . These three new anionic clusters have been isolated as  $\text{PPN}^+$  and/or  $\text{PPh}_4^+$  salts and are formulated on the basis of microanalytical and FAB mass spectrometric data. The solid-state structure of  $[\text{PPh}_4][\text{Re}_6\text{Ir}(\mu_6\text{-C})(\text{CO})_{20}(\mu_3\text{-AuPPh}_3)_2]\cdot\text{CH}_2\text{Cl}_2$  has been determined by X-ray diffraction. Crystal data: triclinic, space group  $P\bar{1}$ ,  $a = 13.1182(1)$  Å,  $b = 15.1806(1)$  Å,  $c = 23.4061(3)$  Å,  $\alpha = 74.251(1)^\circ$ ,  $\beta = 82.058(1)^\circ$ ,  $\gamma = 70.306(1)^\circ$ ,  $Z = 2$ . Further information on the structures of the compounds in solution has been derived from  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR studies.

## Introduction

An important issue in studies of higher-nuclearity transition metal clusters is the controlled manipulation of nuclearity in cluster synthesis.<sup>1–3</sup> For the systematic buildup of clusters, capping of triangular faces of anionic clusters by cationic or neutral mononuclear species has been widely used to form mixed-metal clusters having one or two more metal atoms than the original compounds.<sup>4,5</sup> On the other hand, reactions of metal clusters with carbon monoxide, phosphines, or nitrogen-containing ligands frequently results in the removal of one metal vertex from a higher-nuclearity cluster compound.<sup>6,7</sup>

As part of our continuing study of the synthesis<sup>8</sup> and reactivity<sup>9</sup> of a set of octanuclear mixed-metal clusters with the

general formula  $[\text{Re}_7(\mu_6\text{-C})(\text{CO})_{21}\text{ML}_n]^{2-}$ , we observed that framework rearrangement of 1,4-bicapped  $[\text{Re}_7(\mu_6\text{-C})(\text{CO})_{21}\text{Ir}(\text{CO})_2]^{2-}$  generated  $[\text{Re}_5\text{Ir}(\mu_6\text{-C})(\text{CO})_{17}(\mu_3\text{-Re}(\text{CO})_3)_2]^{2-}$ , a unique 1,3-bicapped isomer.<sup>10</sup> These two structural isomers were used recently as single-source molecular precursors to alumina-supported bimetallic nanoparticles that show catalytically and structurally distinguishable features.<sup>11</sup> In this paper we describe the facile decapping of a  $[\text{Re}(\text{CO})_3]^+$  fragment from  $[\text{Re}_5\text{Ir}(\mu_6\text{-C})(\text{CO})_{17}(\mu_3\text{-Re}(\text{CO})_3)_2]^{2-}$  to give the new cluster trianion  $[\text{Re}_5\text{Ir}(\mu_6\text{-C})(\text{CO})_{17}(\mu_3\text{-Re}(\text{CO})_3)]^{3-}$  as well as further capping reactions of this cluster with the  $[\text{Au}(\text{PPh}_3)]^+$  moiety (see Scheme 1).

## Experimental Section

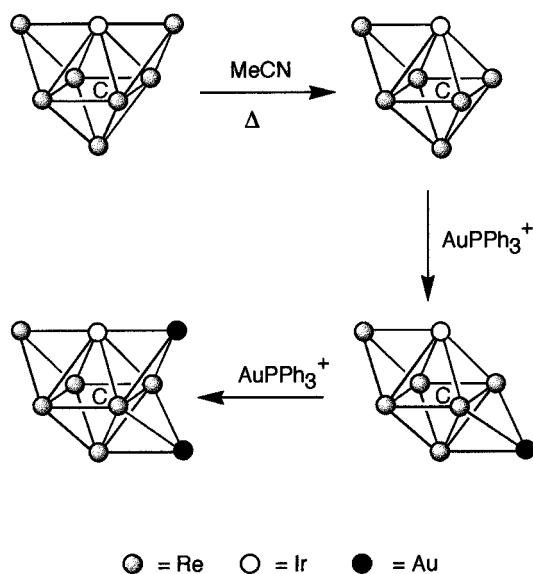
**General Procedures.** All reactions were carried out under a nitrogen atmosphere by using standard Schlenk techniques. All reaction solvents were distilled from appropriate drying agents and degassed immediately before use. The compound  $[\text{PPN}]_2[\text{Re}_5\text{IrC}(\text{CO})_{17}(\mu_3\text{-Re}(\text{CO})_3)_2]$ , including a  $^{13}\text{C}$ -enriched sample, was prepared as previously reported.<sup>10</sup> The compounds  $[\text{PPN}]\text{Cl}$  (Aldrich) and  $\text{Au}(\text{PPh}_3)\text{Cl}$  (Aldrich) were used as received;  $\text{Au}(\text{PPh}_3)\text{NO}_3$  was prepared by a literature method.<sup>12</sup>

IR spectra were recorded with a Perkin-Elmer 1750 FT-IR spectrometer.  $^{13}\text{C}$  NMR spectra were obtained with GE QE-300 and GN-500 spectrometers at 75 and 125 MHz, respectively, using the carbon resonances of deuterated solvents as chemical shift references.  $^{31}\text{P}$  NMR spectra were acquired on a GE GN-300NB instrument at 121.5 MHz and referenced to external 85%  $\text{H}_3\text{PO}_4$ . Negative-ion fast atom bombardment mass spectra (FAB-MS) and elemental analyses were obtained by the respective staffs of the Mass Spectrometry Center and the Microanalytical Laboratory of the School of Chemical Sciences at the University of Illinois.

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## Scheme 1



**Synthesis of [PPN]<sub>2</sub>[Re<sub>5</sub>IrC(CO)<sub>17</sub>(μ<sub>3</sub>-Re(CO)<sub>3</sub>)<sub>2</sub>].** [PPN]<sub>2</sub>[Re<sub>5</sub>IrC(CO)<sub>17</sub>(μ<sub>3</sub>-Re(CO)<sub>3</sub>)<sub>2</sub>] (33.1 mg, 0.0103 mmol) was dissolved in acetonitrile (ca. 30 mL) and the solution heated under reflux for 7 h. After cooling to room temperature, the solution was reduced in volume by half under vacuum. Excess [PPN]Cl (13.5 mg, 0.024 mmol) was added to the solution, which was then thoroughly stirred before the remaining solvent was removed under vacuum. The oily red residue was washed first with chloroform (2 × 3 mL) and then with 2-propanol and finally was dried under reduced pressure to give a red powder (12.3 mg, 34%). Anal. Calcd for C<sub>129</sub>H<sub>90</sub>N<sub>3</sub>IrO<sub>20</sub>P<sub>6</sub>Re<sub>6</sub>: C, 44.30; H, 2.59; N, 1.20. Found: C, 42.19; H, 2.72; N, 1.09. IR (acetone): ν<sub>CO</sub> 2029 (vw), 1976 (s, sh), 1967 (vs), 1952 (w, sh), 1906 (w, sh), 1887 (w) cm<sup>-1</sup>. <sup>13</sup>C NMR (acetone-*d*<sub>6</sub>, 20 °C): δ 415.0 (s, μ<sub>6</sub>-C), 209.3 (s, 3C), 203.6 (s, 3C), 202.2 (s, 6C), 196.2 (s, 6C), 180.3 (s, 2C, Ir–CO). FAB-MS (negative ion): *m/z* (<sup>187</sup>Re, <sup>193</sup>Ir) 2425 (M – 2PPN), 2154 (M – 2PPN – Re(CO)<sub>3</sub>), 1887 (M – 3PPN).

**Synthesis of [PPN]<sub>2</sub>[Re<sub>6</sub>IrC(CO)<sub>20</sub>(AuPPh<sub>3</sub>)<sub>2</sub>] and [PPN][Re<sub>6</sub>IrC(CO)<sub>20</sub>(AuPPh<sub>3</sub>)<sub>2</sub>].** A solution of [Re<sub>6</sub>IrC(CO)<sub>20</sub>]<sup>3-</sup> was prepared in situ by heating an acetonitrile solution of [PPN]<sub>2</sub>[Re<sub>5</sub>IrC(CO)<sub>17</sub>(Re(CO)<sub>3</sub>)<sub>2</sub>] (41.0 mg, 0.0127 mmol) to reflux for 7 h. The solvent was evaporated under vacuum to give a red residue, which was dissolved in dichloromethane (20 mL). Au(PPh<sub>3</sub>)Cl (13.0 mg, 0.0263 mmol) was added to this solution, and the mixture was stirred at room temperature for 24 h; then the solvent was removed in vacuo. Dichloromethane/diethyl ether solvent diffusion was carried out twice on the orange-red residue over a period of 10 days, which provided a red powder of [PPN]<sub>2</sub>[Re<sub>6</sub>IrC(CO)<sub>20</sub>(AuPPh<sub>3</sub>)<sub>2</sub>] (20.1 mg, 46%). Anal. Calcd for C<sub>111</sub>H<sub>75</sub>N<sub>2</sub>Au<sub>2</sub>IrO<sub>20</sub>P<sub>5</sub>Re<sub>6</sub>: C, 39.01; H, 2.21; N, 0.82. Found: C, 38.10; H, 2.32; N, 0.64. IR (acetone): ν<sub>CO</sub> 2041 (vw), 2003 (m), 1989 (vs), 1969 (w), 1911 (w) cm<sup>-1</sup>. <sup>31</sup>P NMR (chloroform-*d*, 20 °C): 78.4 ppm (s, 1P, *P* in AuPPh<sub>3</sub>), 21.8 ppm (s, 4P, *P* in PPN<sup>+</sup>). FAB-MS (negative ion): *m/z* (<sup>187</sup>Re, <sup>193</sup>Ir) 2884 (M – PPN), 2346 (M – 2PPN).

The supernate from the solvent diffusion was evaporated to dryness in vacuo. The orange residue was redissolved in dichloromethane, and *n*-pentane was layered on top. After 2 days at room temperature, red crystals of [PPN][Re<sub>6</sub>IrC(CO)<sub>20</sub>(AuPPh<sub>3</sub>)<sub>2</sub>] (6.2 mg, 15%) were isolated. Anal. Calcd for C<sub>93</sub>H<sub>60</sub>NAu<sub>2</sub>IrO<sub>20</sub>P<sub>4</sub>Re<sub>6</sub>: C, 33.45; H, 1.81; N, 0.42. Found: C, 34.17; H, 2.19; N, 0.48. IR (acetone): ν<sub>CO</sub> 2054 (vw), 2017 (s), 2007 (vs), 2001 (s, sh), 1985 (m), 1942 (w), 1913 (w), 1889 (vw) cm<sup>-1</sup>. <sup>31</sup>P NMR (chloroform-*d*, 20 °C): 82.4 ppm (s, 1P, *P* in AuPPh<sub>3</sub>), 77.6 ppm (s, 1P, *P* in AuPPh<sub>3</sub>), 21.8 ppm (s, 2P, *P* in PPN<sup>+</sup>). FAB-MS (negative ion): *m/z* (<sup>187</sup>Re, <sup>193</sup>Ir) 2805 (M – PPN), 2346 (M – PPN – AuPPh<sub>3</sub>).

**Direct Synthesis of [PPN][Re<sub>6</sub>IrC(CO)<sub>20</sub>(AuPPh<sub>3</sub>)<sub>2</sub>].** An acetonitrile solution containing [Re<sub>6</sub>IrC(CO)<sub>20</sub>]<sup>3-</sup> was prepared in situ from [PPN]<sub>2</sub>[Re<sub>5</sub>IrC(CO)<sub>17</sub>(Re(CO)<sub>3</sub>)<sub>2</sub>] (10.1 mg, 0.00316 mmol) as described

**Table 1.** Crystallographic Data for [PPH<sub>4</sub>]<sub>2</sub>[Re<sub>6</sub>IrC(CO)<sub>20</sub>(AuPPh<sub>3</sub>)<sub>2</sub>]·CH<sub>2</sub>Cl<sub>2</sub>

empirical formula	C <sub>82</sub> H <sub>52</sub> O <sub>20</sub> P <sub>3</sub> Cl <sub>2</sub> Re <sub>6</sub> IrAu <sub>2</sub>
fw	3224.38
space group	<i>P</i> 1̄
temp, (K)	198(2)
<i>a</i> (Å)	13.1182(1)
<i>b</i> (Å)	15.1806(1)
<i>c</i> (Å)	23.4061(3)
α (deg)	74.251(1)
β (deg)	82.058(1)
γ (deg)	70.306(1)
<i>V</i> (Å <sup>3</sup> )	4218.14(7)
<i>Z</i>	2
<i>D</i> <sub>calc</sub> (g·cm <sup>-3</sup> )	2.539
μ(Mo Kα) (cm <sup>-1</sup> )	13.793
λ(Mo Kα) (Å)	0.710 69
<i>F</i> (000)	2936
θ range (deg)	1.47–28.26
no. of refls colld	27 324
no. of indep refls	18 914
<i>R</i> <sub>int</sub>	0.0293
no. of obsd data [ <i>I</i> > 2σ( <i>I</i> )]	18 906
<i>R</i> <sub>1</sub> [ <i>I</i> > 2σ( <i>I</i> )] <sup>a</sup>	0.0426
<i>wR</i> <sub>2</sub> (all data) <sup>b</sup>	0.1387

<sup>a</sup> *R*<sub>1</sub> = Σ|(F<sub>o</sub> – F<sub>c</sub>)/ΣF<sub>o</sub>. <sup>b</sup> *wR*<sub>2</sub> = [Σw(F<sub>o</sub><sup>2</sup> – F<sub>c</sub><sup>2</sup>)/ΣF<sub>o</sub><sup>4</sup>]<sup>1/2</sup> with *w* = 1/[σ<sup>2</sup>(F<sub>o</sub><sup>2</sup>) + (0.0632*p*)<sup>2</sup> + 100.7129*p*] where *p* = (F<sub>o</sub><sup>2</sup> + 2F<sub>c</sub><sup>2</sup>)/3.

above. The solvent was evaporated under vacuum, and the red residue was redissolved in dichloromethane (5 mL). Solid Au(PPh<sub>3</sub>)NO<sub>3</sub> (3.55 mg, 0.00681 mmol) was added to the deep red solution, which changed instantly to orange-red. The solution was stirred for 3 h and then evaporated under vacuum. A dichloromethane solution of the residue layered with diethyl ether provided red crystals of [PPN][Re<sub>6</sub>IrC(CO)<sub>20</sub>(AuPPh<sub>3</sub>)<sub>2</sub>] (5.7 mg, 55%) after 1 week. The [PPH<sub>4</sub>]<sup>+</sup> salt was prepared in a similar manner.

**X-ray Crystallographic Study of [PPH<sub>4</sub>]<sub>2</sub>[Re<sub>6</sub>IrC(CO)<sub>20</sub>(AuPPh<sub>3</sub>)<sub>2</sub>].** Single crystals of the compound suitable for X-ray crystallography were grown by dichloromethane/hexane solvent diffusion at room temperature in the course of 2 days. The red, columnar crystal (0.14 × 0.20 × 0.40 mm<sup>3</sup>) was mounted to a thin glass fiber by using oil (Paratone-N, Exxon), and diffraction data were collected on a Siemens Platform/CCD automated diffractometer at 198 K. The 18 914 independent reflections (with maximum 0.2063 and minimum 0.0169 transmission) were corrected numerically for absorption. A summary of crystallographic details is given in Table 1.

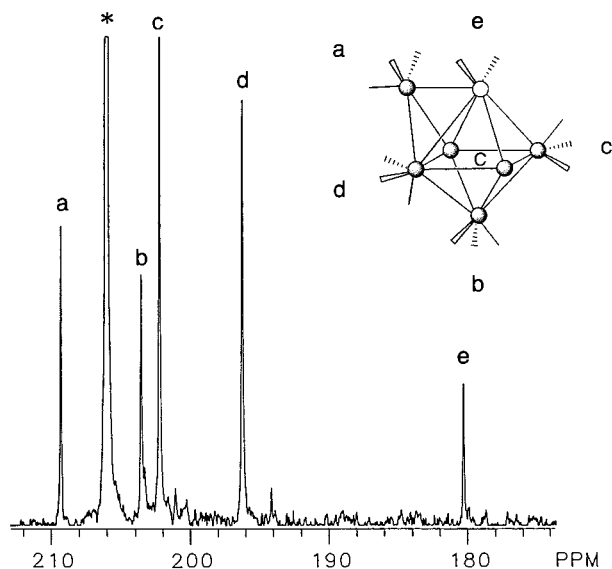
The structure was solved by direct methods (SHELXTL);<sup>13</sup> hydrogen atoms were fixed on calculated positions. Full-matrix least-squares refinement, based on *F*<sup>2</sup>, of the positional and anisotropic thermal parameters for all non-hydrogen atoms converged at *R*<sub>1</sub> = 0.0426 (*wR*<sub>2</sub> = 0.1114) for those data with *I* > 2σ(*I*). Complete details of the crystallographic study and atomic coordinates for [PPH<sub>4</sub>]<sub>2</sub>[Re<sub>6</sub>IrC(CO)<sub>20</sub>(AuPPh<sub>3</sub>)<sub>2</sub>] are provided as Supporting Information. Selected bond lengths and angles for the cluster molecule are given in Table 2.

## Results and Discussion

**Formation and Characterization of [Re<sub>6</sub>IrC(CO)<sub>20</sub>]<sup>3-</sup>.** When [PPN]<sub>2</sub>[Re<sub>5</sub>Ir(μ<sub>6</sub>-C)(CO)<sub>17</sub>(μ<sub>3</sub>-Re(CO)<sub>3</sub>)<sub>2</sub>] is heated in refluxing acetonitrile for several hours, the new complex [Re<sub>6</sub>IrC(CO)<sub>20</sub>]<sup>3-</sup> is formed, presumably together with [Re(CO)<sub>3</sub>(NCCCH<sub>3</sub>)<sub>3</sub>]<sup>+</sup>, which has not been identified. The solution IR (ν<sub>CO</sub>) spectrum of the new cluster is very similar to that of [Re<sub>7</sub>C(CO)<sub>21</sub>]<sup>3-</sup>,<sup>14</sup> supporting its formulation as a trianion. The negative-ion FAB mass spectrum of the isolated PPN<sup>+</sup> salt shows the highest mass multiplets centered at *m/z* 2420, which

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**Figure 1.**  $^{13}\text{C}$  NMR spectrum (carbonyl region, acetone- $d_6$ , 20 °C) of  $[\text{PPN}]_3[\text{Re}_6\text{IrC}(\text{CO})_{20}]$ . The asterisk denotes a solvent resonance.

**Table 2.** Selected Structural Parameters for  $[\text{PPh}_4]_2[\text{Re}_6\text{IrC}(\text{CO})_{20}(\text{AuPPh}_3)_2]$

Bond Distances (Å)					
Au1–Ir1	2.758(1)	Au1–Re2	2.944(1)	Au1–Re3	2.922(1)
Au2–Re2	2.890(1)	Au2–Re3	2.897(1)	Au2–Re6	2.844(1)
Ir1–Re2	3.020(1)	Ir1–Re3	3.026(1)	Ir1–Re7	2.816(1)
Ir1–Re4	2.859(1)	Ir1–Re5	2.867(1)	Re4–Re5	3.007(1)
Re2–Re3	2.982(1)	Re2–Re6	3.161(1)	Re3–Re6	3.103(1)
Re4–Re3	3.061(1)	Re4–Re6	2.982(1)	Re4–Re7	2.977(1)
Re5–Re2	3.050(1)	Re5–Re6	3.012(1)	Re5–Re7	2.951(1)
Ir1–C	2.11(1)	Re2–C	2.18(1)	Re3–C	2.15(1)
Re4–C	2.11(1)	Re5–C	2.13(1)	Re6–C	2.10(1)
Au1–P1	2.293(2)	Au2–P2	2.304(3)		
Bond Angles (deg)					
P1–Au1–Ir1	134.95(8)	P1–Au1–Re2	152.02(8)		
P1–Au1–Re3	140.58(8)	P2–Au2–Re2	140.81(8)		
P2–Au2–Re3	143.79(8)	P2–Au2–Re6	140.75(8)		

corresponds to the formula  $[\text{PPN}][\text{Re}_6\text{IrC}(\text{CO})_{20}]^-$ . However, since we have not been able to obtain the compound in crystalline form suitable for X-ray diffraction, we have used  $^{13}\text{C}$  NMR spectroscopy for structural elucidation.

The  $^{13}\text{C}$  NMR spectrum of  $[\text{Re}_6\text{IrC}(\text{CO})_{20}]^{3-}$  shows a carbide resonance at  $\delta$  415, which is in the expected range.<sup>8,9,14</sup> The carbonyl region of the spectrum is shown in Figure 1. There are five carbonyl signals at  $\delta$  209.3, 203.6, 202.2, 196.2, and 180.3, with 3:3:6:6:2 relative intensities. This pattern is expected for a  $C_s$ -symmetric monocapped octahedral structure derived by the removal of a  $\text{Re}(\text{CO})_3^+$  capping moiety from  $[\text{Re}_5\text{Ir}(\mu_6\text{-C})(\text{CO})_{17}(\mu_3\text{-Re}(\text{CO})_3)_2]^{2-}$ . Although the same pattern of relative intensities could be generated at low temperatures by a 3-fold symmetric structure with the  $\text{Ir}(\text{CO})_2$  moiety in a capping position, we would expect local carbonyl rotation to be fast at room temperature,<sup>8</sup> which would lead to a 9:9:2 pattern. Furthermore, since the structure of the digold derivative (vide infra) shows the Ir center as part of the  $M_6(\mu_6\text{-C})$  core, the iridium atom is most likely in this position in  $[\text{Re}_6\text{IrC}(\text{CO})_{20}]^{3-}$  as well.

We assign the highest frequency carbonyl signal in Figure 1 to the three carbonyls **a** on the capping rhenium, because in heptarhenium-based clusters this signal always appears more highly shifted than the rest of the carbonyl resonances,<sup>8,14</sup> and the substitution of an iridium atom for a rhenium atom in an adjacent position should not change this trend significantly. The

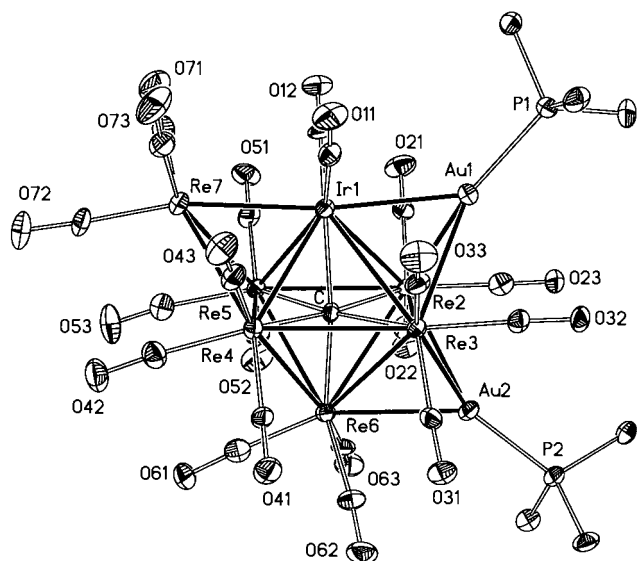
other signal of intensity 3C is then assigned by default to the carbonyls **b** on the unique rhenium atom residing in the symmetry plane. We assign the signal at 202.2 ppm to the six carbonyls **c** attached to the two rhenium atoms on the open face and the resonance at 196.2 ppm to the six carbonyls **d** on the two rhenium atoms forming part of the face capped by  $\text{Re}(\text{CO})_3$ . This assignment is consistent with that of Hayward<sup>14</sup> for the analogous carbonyl positions in  $[\text{Re}_7\text{C}(\text{CO})_{21}]^{3-}$ . Finally, we attribute the low-frequency signal of intensity 2C to the two iridium-bound carbonyls **e**, on the basis of chemical shift and intensity.<sup>10</sup>

The removal of a  $[\text{Re}(\text{CO})_3]^+$  capping group from a capped  $\text{Re}_6(\mu_6\text{-C})$  core has been observed in a number of cluster systems.<sup>6b,7,15</sup> Since loss of the cationic species formally increases the negative charge on the remaining cluster, this process typically proceeds readily when the change in charge is from 1– to 2–. Illustrative examples include (i)  $[\text{Re}_6\text{C}(\text{CO})_{19}]^{2-}$  from  $[\text{Re}_7\text{C}(\text{CO})_{22}]^-$  with CO,<sup>6b</sup> (ii)  $[\text{Re}_6\text{C}(\text{CO})_{19}]^{2-}$  from  $[\text{Re}_7\text{C}(\text{CO})_{21}\text{P}(\text{OPh})_3]^-$  with CO,<sup>7b</sup> (iii)  $[\text{Re}_6\text{C}(\text{CO})_{18}(\text{CH}_2)]^{2-}$  from  $[\text{Re}_7\text{C}(\text{CO})_{21}(\text{CH}_2)]^-$  with  $\text{NCCH}_3$ ,<sup>7c</sup> and (iv)  $[\text{H}_2\text{Re}_6\text{C}(\text{CO})_{18}]^{2-}$  from  $[\text{H}_2\text{Re}_7\text{C}(\text{CO})_{21}]^-$  with  $\text{NCCH}_3$ .<sup>15</sup> The only previous report involving such rhenium clusters, in which a trianion was formed in an obvious decapping reaction, viz., the conversion of  $[\text{Re}_8\text{C}(\text{CO})_{24}]^{2-}$  to  $[\text{Re}_7\text{C}(\text{CO})_{21}]^{3-}$ ,<sup>14</sup> required strongly reducing conditions (sodium/diglyme). Thus, the relative ease of the decapping reaction in acetonitrile that converts  $[\text{Re}_5\text{IrC}(\text{CO})_{17}(\mu_3\text{-Re}(\text{CO})_3)_2]^{2-}$  to  $[\text{Re}_5\text{IrC}(\text{CO})_{17}(\mu_3\text{-Re}(\text{CO})_3)]^{3-}$  is remarkable.

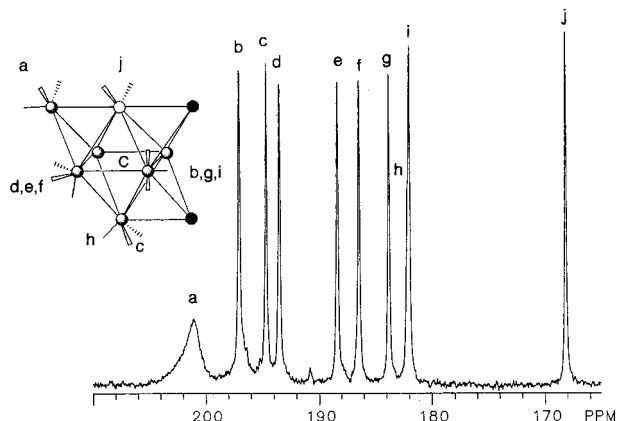
**Capping of  $[\text{Re}_6\text{IrC}(\text{CO})_{20}]^{3-}$  by the  $[\text{AuPPh}_3]^+$  Moiety.** The charge and structural similarities between  $[\text{Re}_7\text{C}(\text{CO})_{21}]^{3-}$  and  $[\text{Re}_6\text{IrC}(\text{CO})_{20}]^{3-}$  led us to explore with the new cluster a capping reaction with the coinage metal fragment  $[\text{AuPPh}_3]^+$  as we had done previously with the former cluster.<sup>8a</sup> The reaction of  $[\text{Re}_6\text{IrC}(\text{CO})_{20}]^{3-}$  with 1.1 equiv of  $\text{Au}(\text{PPh}_3)\text{Cl}$  in dichloromethane is complete after 14 h at room temperature. The major IR band observed shifts from 1971  $\text{cm}^{-1}$  for the starting material to 1987  $\text{cm}^{-1}$  for the product, which compares with 1992  $\text{cm}^{-1}$  for  $[\text{Re}_7\text{C}(\text{CO})_{21}(\text{AuPPh}_3)]^{2-}$ .<sup>8a</sup> The FAB mass spectrum of the isolated  $[\text{PPN}]^+$  salt is fully consistent with the formula  $[\text{Re}_6\text{IrC}(\text{CO})_{20}(\text{AuPPh}_3)]^{2-}$ .

When excess  $\text{Au}(\text{PPh}_3)\text{Cl}$  (> 2 equiv) is added to a dichloromethane solution of  $[\text{Re}_6\text{IrC}(\text{CO})_{20}]^{3-}$ , and the reaction is allowed to proceed for more than a day at room temperature, a different species is observed in the IR spectrum, with two strong bands at 2017 and 2007  $\text{cm}^{-1}$ . From this reaction mixture, isolation of the  $\text{PPN}^+$  salt of this new species by solvent interdiffusion proceeds only in low yield, but the new cluster anion is readily formulated as  $[\text{Re}_6\text{IrC}(\text{CO})_{20}(\text{AuPPh}_3)_2]^-$  on the basis of its FAB mass spectrum. It appears that the low yield of digold product from this procedure is due to both monogold and digold compounds coexisting in the reaction mixture. Thus, when a second equivalent of  $\text{Au}(\text{PPh}_3)\text{Cl}$  is added to a dichloromethane solution of  $[\text{Re}_6\text{IrC}(\text{CO})_{20}(\text{AuPPh}_3)]^{2-}$ , complete conversion to  $[\text{Re}_6\text{IrC}(\text{CO})_{20}(\text{AuPPh}_3)_2]^-$  is very slow, requiring ca. 7 days at room temperature. Furthermore, when the digold complex is treated with excess  $[\text{PPN}]\text{Cl}$  (ca. 50 eq), it gradually loses one gold capping group to give the monogold complex over a period of several days. Therefore, chloride is best avoided in advance, and the digold derivative is synthesized cleanly and efficiently by treating  $[\text{Re}_6\text{IrC}(\text{CO})_{20}]^{3-}$  with 2 equiv of  $[\text{AuPPh}_3]\text{NO}_3$ . Similar gold cap abstraction by chloride has been observed for  $[\text{Rh}_6\text{C}(\text{CO})_{13}]^{3-}$

(15) Beringhelli, T.; D'Alfonso, G.; Ciani, G.; Sironi, A.; Molinari, H. *J. Chem. Soc., Dalton Trans.* **1990**, 1901.



**Figure 2.** ORTEP diagram of the molecular structure of  $[\text{Re}_6\text{IrC}(\text{CO})_{20}(\text{AuPPh}_3)_2]^-$  with 35% thermal ellipsoids. Only the ipso carbons of the phenyl groups are depicted.

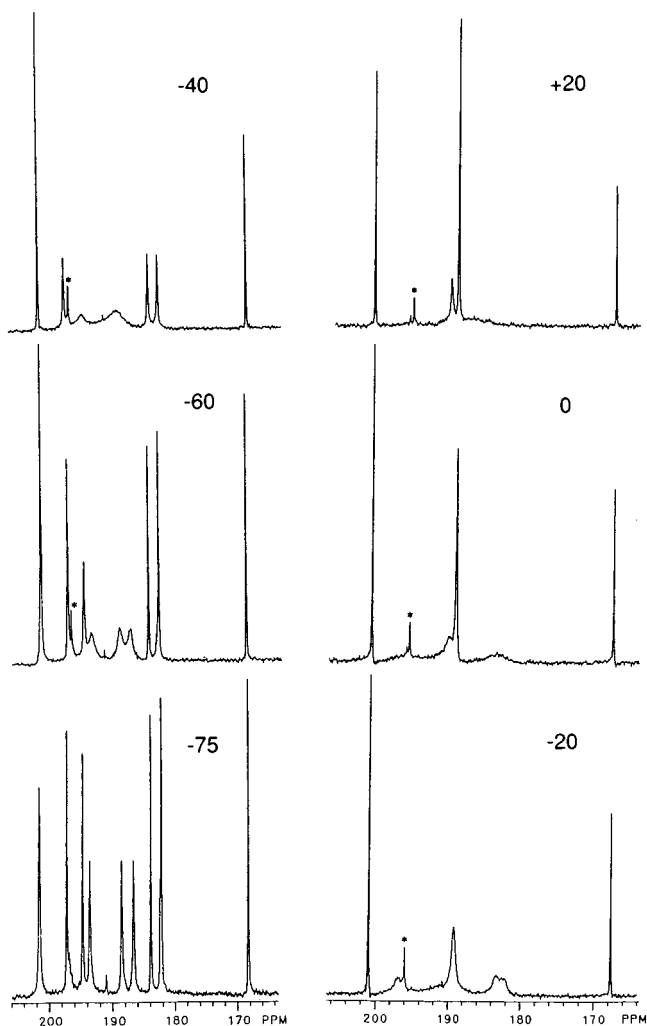


**Figure 3.**  $^{13}\text{C}$  NMR spectrum (carbonyl region, dichloromethane- $d_2$ ,  $-95\text{ }^\circ\text{C}$ ) of  $[\text{PPN}][\text{Re}_6\text{IrC}(\text{CO})_{20}(\text{AuPPh}_3)_2]$ .

$(\text{AuPPh}_3)_2]$ ,<sup>4d</sup>  $[\text{Ir}_6(\text{CO})_{15}(\text{AuPPh}_3)]^-$ ,<sup>4e</sup> and  $[\text{HRe}_6\text{C}(\text{CO})_{18}(\text{AuPPh}_3)_2]^-$ .<sup>16</sup>

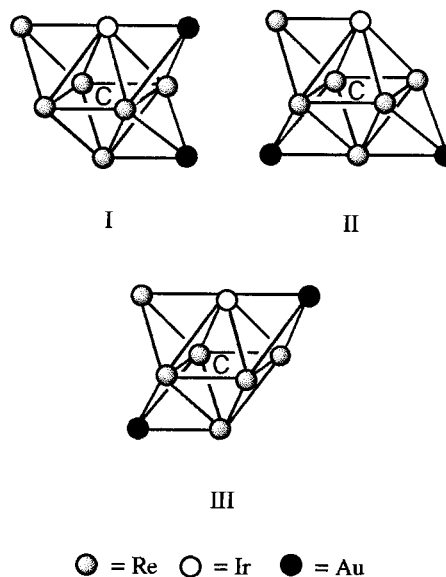
**X-ray Crystallographic Study of  $[\text{Re}_6\text{IrC}(\text{CO})_{20}(\text{AuPPh}_3)_2]^-$ .** Figure 2 shows a diagram of the molecule with the crystallographic labeling scheme. The structure of the digold cluster consists of an  $\text{Re}_5\text{Ir}$  octahedral core containing an interstitial carbide and capped on three faces with two  $\text{AuPPh}_3$  fragments and one  $\text{Re}(\text{CO})_3$  unit. All metal atoms of the three capping moieties lie together with Ir1, Re6, and the carbide carbon atom on a pseudosymmetry plane. The gold fragment Au1 caps the face defined by Ir1, Re2, and Re3, the second fragment Au2 is bonded to Re2, Re3, and Re6, and the  $\text{Re}(\text{CO})_3$  cap is located on the face (Ir1, Re4, and Re5) opposite to the one capped by Au2.

A survey of the metal–metal bond distances (Table 2) reveals that there is a pattern in their variation. The two bonds Ir1–Re2 and Ir1–Re3 on the Au1-capped face are longer than the remaining three Ir–Re bonds. Also, the two bonds Re2–Re6 and Re3–Re6 on the Au2-capped face are longer than all other Re–Re bonds, including the Re2–Re3 bond between the two gold caps. This pattern shows that the two gold fragments move



**Figure 4.** Variable-temperature  $^{13}\text{C}$  NMR spectra (carbonyl region, dichloromethane- $d_2$ ) of  $[\text{PPN}][\text{Re}_6\text{IrC}(\text{CO})_{20}(\text{AuPPh}_3)_2]$ . Indicated temperatures are in  $^\circ\text{C}$ . The asterisk marks an impurity.

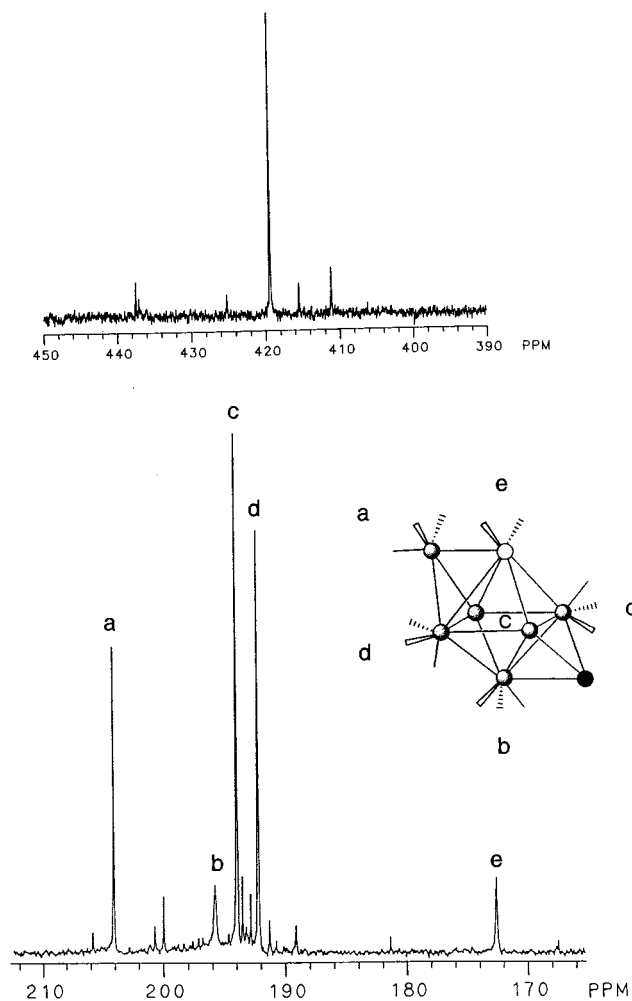
### Chart 1



away from each other, pushing Ir1 and Re6 away from the edge defined by the Re2–Re3 vector. This conclusion is also supported by the observed angles  $\text{Re}_x\text{--Au}_y\text{--P}_y$ .

The ability of  $[\text{Re}_6\text{IrC}(\text{CO})_{20}]^{3-}$  to allow bicapping by the

(16) Latten, J. L.; Hsu, G.; Henly, T. J.; Wilson, S. R.; Shapley, J. R. *Inorg. Chem.* **1998**, *37*, 2520.

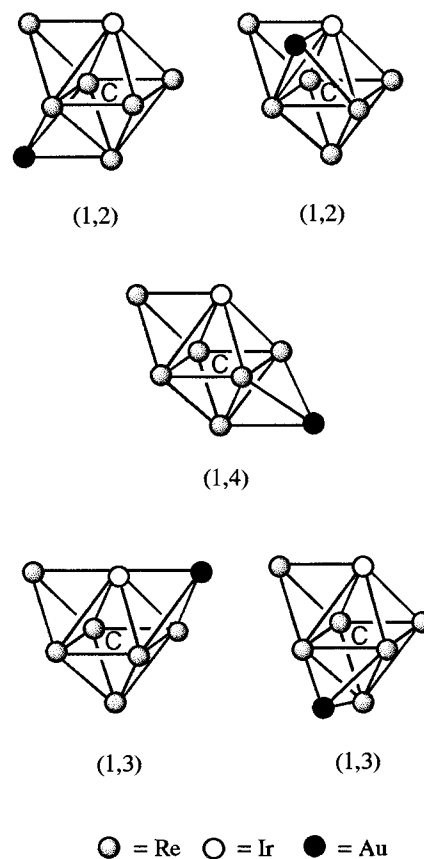


**Figure 5.**  $^{13}\text{C}$  NMR spectra of  $[\text{PPN}]_2[\text{Re}_6\text{IrC}(\text{CO})_{20}(\text{AuPPh}_3)]$  in dichloromethane- $d_2$ : top, carbide region,  $-95\text{ }^\circ\text{C}$ ; bottom, carbonyl region,  $20\text{ }^\circ\text{C}$ .

$[\text{AuPPh}_3]^+$  fragment is quite interesting. In the case of  $[\text{Re}_7\text{C}(\text{CO})_{21}]^{3-}$ , only the monogold complex was observed;<sup>8a</sup> however, a digold derivative has been characterized for  $[\text{HRe}_6\text{C}(\text{CO})_{18}]^{3-}$ .<sup>16</sup> Neutral digold derivatives are known for  $[\text{Os}_6(\text{CO})_{18}]^{2-}$ ,<sup>4b</sup>  $[\text{Ru}_6\text{C}(\text{CO})_{16}]^{2-}$ ,<sup>17</sup> and  $[\text{Rh}_6\text{C}(\text{CO})_{13}]^{2-}$ ,<sup>4d</sup> but the  $\text{M}_6\text{Au}_2$  framework geometries vary considerably: the  $\text{Os}_6$  compound has trans face-bridging Au groups, the  $\text{Ru}_6$  compound has trans edge-bridging Au groups, and the  $\text{Rh}_6$  compound has cis face-bridging Au groups that develop a gold-gold bond. It is not clear how dramatically we should expect the replacement of a rhenium atom in  $[\text{Re}_7\text{C}(\text{CO})_{21}]^{3-}$  by an iridium atom in  $[\text{Re}_6\text{IrC}(\text{CO})_{20}]^{3-}$  to change the bonding ability of the heptanuclear framework toward two  $[\text{AuPPh}_3]^+$  caps. On the basis of IR spectra,  $[\text{Re}_6\text{IrC}(\text{CO})_{20}]^{3-}$  and  $[\text{Re}_7\text{C}(\text{CO})_{21}]^{3-}$  have very similar electron densities (1978 and  $1971\text{ cm}^{-1}$  vs 1977 and  $1968\text{ cm}^{-1}$ , respectively). Nevertheless, the decrease in the number of carbonyl ligands by 1 in  $[\text{Re}_6\text{IrC}(\text{CO})_{20}]^{3-}$  does open up more space for gold binding to the cluster core, and this may be sufficiently decisive to allow bicapping.

**$^{13}\text{C}$  and  $^{31}\text{P}$  NMR Studies.** The room-temperature  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $[\text{Re}_6\text{IrC}(\text{CO})_{20}(\text{AuPPh}_3)_2]^-$  contains two sharp singlets of 1:1 ratio at 82.4 and 77.5 ppm due to two

**Chart 2**



$\text{AuPPh}_3$  environments. The  $^{13}\text{C}$  NMR spectrum has only one carbide resonance at  $\delta\ 415.5$  throughout the temperature range of  $-95$  to  $+20\text{ }^\circ\text{C}$ . The spectrum at  $-95\text{ }^\circ\text{C}$  shows 10 signals in the carbonyl region with a ratio of 3:2:2:2:2:2:2:1:2:2, which are labeled sequentially from **a** to **j** (see Figure 3). The three structures shown in Chart 1 all have  $C_3$  symmetry, and all would allow observation of 2  $^{31}\text{P}$  and 10 carbonyl  $^{13}\text{C}$  NMR signals. Our specific choice of structure **I** is dependent upon the solid-state structure study.

The 10 carbonyl signals can be placed in the following groups on the basis of their temperature-dependent behavior (see Figure 4): **a** (3C); **b**, **g**, **i** (6C); **c**, **h** (3C); **d**, **e**, **f** (6C); **j** (2C). The dynamic process is assumed to be local 3-fold rotation at each rhenium center, and the specific assignments are based on the assumption that the activation barrier to this process will increase with the coordination number of the rhenium atom. Thus, the signals for carbonyls **a** on capping Re7 are just above coalescence at  $-95\text{ }^\circ\text{C}$  and are already in fast exchange at  $-75\text{ }^\circ\text{C}$ . At this point, resonances **d**, **e**, and **f** are beginning to broaden and collapse together. Resonances **c** and **h** are the next to start observable exchange at  $-60\text{ }^\circ\text{C}$ , and they are assigned to the three carbonyls on Re6 attached to Au2. Finally, resonances **b**, **g**, and **i** show the onset of exchange at  $-40\text{ }^\circ\text{C}$ , and they are assigned to the six carbonyls on the two rhenium atoms Re2 and Re3 attached to both gold atoms. Finally, the signal **j** at highest field is clearly due to the two carbonyls on the iridium center. At room temperature, each of the sets of carbonyls shows a distinct signal, except that for **b**, **g**, and **i**, which is still broad and barely observable above the baseline, and there is no evidence for carbonyl scrambling between metal atoms.

The room-temperature  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of the monogold cluster  $[\text{Re}_6\text{IrC}(\text{CO})_{13}(\text{AuPPh}_3)]^{2-}$  contains a singlet

(17) (a) Bruce, M. I.; Horn, E.; Humphrey, P. A.; Tiekink, E. R. T. *J. Organomet. Chem.* **1996**, *518*, 121. (b) Bunkhall, S. R.; Holden, H. D.; Johnson, B. F. G.; Lewis, J.; Pain, G. N.; Raithby, P. R.; Taylor, M. J. *J. Chem. Soc., Chem. Commun.* **1984**, 25.

at 78.4 ppm, assigned to the AuPPh<sub>3</sub> unit. Of course, this one signal does not specify the structure, since it could be due either to a single species or to several species undergoing fast exchange. The <sup>13</sup>C NMR spectrum at –95 °C in the carbide region is quite informative, with the observation of five resonances, a dominant signal at δ 419.3 together with four weaker signals between δ 437 and 411. This spectrum is shown in the top part of Figure 5. The weak signal at δ 415.5 is attributed to the presence of a small amount of the digold compound. The origin of the different carbide signals is presumably due to isomers in which the gold capping moiety occupies the five different types of triangular faces, i.e., two (1,2), two (1,3), and one (1,4) with respect to the capping Re(CO)<sub>3</sub> group, all of which are shown in Chart 2. At –95 °C, the carbonyl region between δ 210 and 180 in the <sup>13</sup>C NMR spectrum is very complex, preventing an accurate assignment of the resonances. Spectra taken at temperatures between –95 and +20 °C show the gradual diminution of the carbonyl signals due to the minor isomers and the coalescence of the rhenium-bound-carbonyl signals of the major isomer. At 20 °C the carbonyl region of the spectrum consists mainly of a prominent 3:3:6:6:2 pattern, as shown in the bottom part of Figure 5. This pattern is consistent with any of the three C<sub>s</sub>-symmetric structures shown in Chart 2, i.e., one 1,2 isomer, one 1,3 isomer, and the 1,4 isomer. However, the specific chemical shifts of the rhenium carbonyls are very close to those recorded for 1,4-bicapped [Re<sub>7</sub>C(CO)<sub>21</sub>(AuPPh<sub>3</sub>)<sub>2</sub>]<sup>2–</sup>,<sup>8a</sup> so we prefer a 1,4 structure for the major isomer of [Re<sub>6</sub>IrC(CO)<sub>13</sub>(AuPPh<sub>3</sub>)<sub>2</sub>]<sup>2–</sup> as well. This assignment places the gold atom in the position of Au2 in the

crystal structure of the digold derivative (see Figure 2). It is likely that a second isomer of significant stability would have the gold atom in the position of Au1 adjacent to the iridium center, i.e., the 1,3 isomer with a mirror plane, since this is the metal atom configuration for the Re(CO)<sub>3</sub>-capped analogue, namely, [Re<sub>5</sub>IrC(CO)<sub>17</sub>(μ<sub>3</sub>-Re(CO)<sub>3</sub>)<sub>2</sub>]<sup>2–</sup>.

### Conclusions

The trianion cluster [Re<sub>5</sub>IrC(CO)<sub>17</sub>(μ<sub>3</sub>-Re(CO)<sub>3</sub>)<sub>2</sub>]<sup>3–</sup> is readily formed by loss of a [Re(CO)<sub>3</sub>]<sup>+</sup> cap from the dianion [Re<sub>5</sub>IrC(CO)<sub>17</sub>(μ<sub>3</sub>-Re(CO)<sub>3</sub>)<sub>2</sub>]<sup>2–</sup> in refluxing acetonitrile. Adding [AuPPh<sub>3</sub>]<sup>+</sup> caps to the trianion gives both monogold and digold derivatives. The digold complex [Re<sub>5</sub>IrC(CO)<sub>20</sub>(AuPPh<sub>3</sub>)<sub>2</sub>]<sup>–</sup> shows only one structure in the solid state and in solution, whereas several isomers of the monogold complex [Re<sub>6</sub>IrC(CO)<sub>20</sub>(AuPPh<sub>3</sub>)<sub>2</sub>]<sup>2–</sup> are observed in solution.

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**Supporting Information Available:** An X-ray crystallographic file, in CIF format, for [PPh<sub>4</sub>][Re<sub>6</sub>IrC(CO)<sub>20</sub>(AuPPh<sub>3</sub>)<sub>2</sub>]·CH<sub>2</sub>Cl<sub>2</sub> is available on the Internet only. Access information is given on any current masthead page.

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