

angle (116° in **1a,b**; 109.3° in **9**) accompanying Ir-Ir bond formation to force the N atoms somewhat toward tetrahedral geometry. Intramolecular contacts are significant (~3.2 Å) in one region of molecule **9**, between the chloropyrazolyl bridges and phenyl rings C(31)-C(36) and C(61)-C(66). This twists the bridging ligands with respect to the Ir-Ir bond, causing Ir(1) to deviate 0.16 and 0.61 Å from the two pyrazolyl planes with Ir(2) so displaced by 0.52 and 0.23 Å.

Reaction of complex **1** with methyl iodide (1 equiv or excess) afforded a 1:1 adduct as a yellow powder (**10**), which like **7** and **8** showed poor solubility in organic solvents. Two  $\nu_{\text{CO}}$  absorptions were found in the IR spectrum at 2013 and 1993  $\text{cm}^{-1}$ , and the  $^{31}\text{P}$  NMR spectrum consisted of two resonances having equal intensity (-140.5, -141.8 ppm) attributable to  $\text{PPh}_3$  ligands attached to distinguishable metal atoms. These data indicate a structure similar to **C**, with Me and I in apical positions at Ir as has been established crystallographically<sup>1a</sup> for the MeI adduct of complex **2**. By contrast, a corresponding reaction with MeBr appeared to give several products, and a bromo analogue of **10** has not yet been isolated. These observations will be consolidated as part of a more extensive examination of the reactivity of compound **1** toward functionalized organic molecules.

There is a close stereochemical relationship between the structures of compounds **1** and **9**. Both are enantiomeric ( $C_2$

molecular symmetry) and share the same (trans) orientation of terminal ligands in the equatorial plane at Ir, i.e. the oxidative addition step occurs with no net ligand reorganization at the metal center. The dimer (**1**) and related complexes are in principle resolvable, either by incorporation of a chiral phosphine or related ligand or via diastereomer formation involving successive oxidative addition/reductive elimination of an optically pure substrate. Access to such resolved complexes and their relevance to reactions involving asymmetric induction or chiral recognition is being investigated.

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**Registry No.** **1a**, 80461-91-2; **1b**, 92283-13-1; **2**, 80462-13-1; **7**, 80462-14-2; **8**, 80462-15-3; **9**, 80461-90-1; **10**, 80471-11-0; *trans*- $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ , 15318-31-7;  $[\text{Ir}(\text{C}_8\text{H}_{12})\text{Cl}]_2$ , 12112-67-3;  $\text{I}_2$ , 7553-56-2;  $\text{Br}_2$ , 7726-95-6;  $\text{Cl}_2$ , 7782-50-5; Ir, 7439-88-5; methyl iodide, 74-88-4; methyl bromide, 74-83-9; pyrazole, 288-13-1.

**Supplementary Material Available:** Listings of thermal parameters, anisotropic and isotropic temperature factors, least-squares planes, bond lengths and bond angles, and observed and calculated structure factors for compounds **1a**, **1b**, and **9** (51 pages). Ordering information is given on any current masthead page.

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## Synthesis and Spectroscopic Studies of Metal-Metal-Bonded Linear Heterotrimetallic Gold(I) Complexes. Crystal Structure of $[n\text{-Bu}_4\text{N}][\text{Au}[\text{Cr}(\text{CO})_3\text{-}\eta\text{-C}_5\text{H}_5]_2]$

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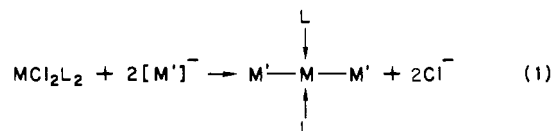
A series of heterotrimetallic Au(I) anionic complexes of the general formula  $[\text{M}'\text{-Au-M}']^-$  with  $\text{M}' = \text{Mn}(\text{CO})_5$  (**1**),  $\text{Co}(\text{CO})_4$  (**2**),  $\text{Cr}(\text{CO})_3\text{Cp}$  (**3**),  $\text{Mo}(\text{CO})_3\text{Cp}$  (**4**),  $\text{W}(\text{CO})_3\text{Cp}$  (**5**), and  $\text{Fe}(\text{CO})_2\text{Cp}$  (**6**) have been prepared and characterized. The linear coordination about the gold atom is evidenced by infrared spectroscopy, particularly in the metal-metal stretching region where a strong absorption between 150 and 200  $\text{cm}^{-1}$  is typical for the  $\nu_{\text{as}}(\text{Au-M}')$  vibration. The corresponding approximate force constants are compared with those of other related linear trimetallic complexes. It is found that metal-metal bond strength increases in the  $\text{M}'\text{-M-M}'$  systems in the following sequence of  $\text{M} = \text{Pd} < \text{Pt} < \text{Au} < \text{Hg}$ . The same trend is observed for the covalency of these complexes as deduced from their  $\nu(\text{CO})$  frequencies. The molecular structure of  $[n\text{-Bu}_4\text{N}][\text{Au}[\text{Cr}(\text{CO})_3\text{Cp}]_2]$  (**3**) has been determined by X-ray diffraction:  $P2_1/c$  with  $a = 1110.6$  (6) pm,  $b = 1690.5$  (14) pm,  $c = 2209.2$  (8) pm,  $\beta = 122.46$  (3)°, and  $Z = 4$ . The complex anion has approximate  $C_2$  symmetry. The Cr(1)-Au-Cr(2) angle is 162.2 (3)°, and the Au-Cr distances are 264.1 (9) and 263.5 (8) pm. The coordination about the Cr atoms is of the "four-legged piano-stool" type. The  $^{197}\text{Au}$  Mössbauer parameters of **1**, **4**, and **6** have been measured and are compared with those obtained for  $\text{AuCl}_2^-$  and  $\text{AuI}_2^-$ . Considering the linearity of these molecules, the IS and QS values are consistent with complexes in which the Au(I) center has a  $sp$  hybridization. They furthermore confirm the bonding scheme deduced from infrared spectroscopy, in which  $\sigma$  bonding between the metals is predominant and  $\pi$  effects will arise from  $\pi$  donation into the gold  $6p_x$  and  $6p_y$  orbitals.

### Introduction

Polymetallic complexes in which the metal atoms are connected to each other through metal-metal bonds only form now a well-known class in organometallic chemistry.<sup>1,2</sup> Previously, we have shown that the reaction of carbonylmetalates,  $[\text{M}']^-$  with cis or trans square-planar palladium or platinum halide complexes can be successfully applied to the synthesis of heterotrimetallic chain complexes (eq 1).<sup>3-7</sup>

Such complexes are of interest for numerous reasons:

(i) They contribute to a better knowledge of the role of metal-metal bonding in stabilizing polymetallic complexes



$\text{M} = \text{Pd}, \text{Pt}; \text{L} = \text{py}^3, \text{RNC}^4, \text{RCN}^6, \text{CO}^6, \text{M}' = \text{Mn}(\text{CO})_5, \text{Co}(\text{CO})_4, \text{Fe}(\text{CO})_3\text{NO}, \text{Cr}(\text{CO})_3\text{Cp}, \text{Mo}(\text{CO})_3\text{Cp}, \text{W}(\text{CO})_3\text{Cp}$  ( $\text{Cp} = \eta\text{-C}_5\text{H}_5$ )

since, in these examples, their cohesion is achieved without the assistance of bridging ligands. This proved to be partic-

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ularly informative in the case where M is palladium since the isolation and characterization of the first complexes containing a palladium-transition metal bond were carried out with *trans*-Pd[Mo(CO)<sub>3</sub>Cp]<sub>2</sub>(py)<sub>2</sub>,<sup>3a</sup> *trans*-Pd[Co(CO)<sub>4</sub>]<sub>2</sub>(py)<sub>2</sub>, and *trans*-Pd[Mn(CO)<sub>5</sub>]<sub>2</sub>(py)<sub>2</sub>.<sup>3b</sup> It provided evidence that these heteronuclear metal-metal bonds were intrinsically strong enough to confer to these molecules a reasonable thermodynamic stability, although their reactivity is high.

(ii) The different nature of the metals constituting the M'-M-M' chain introduces intrinsic polarity into the metal-metal bonds. Thus, in complexes of eq 1, we have spectroscopically established that the 16-electron center M is electrophilic whereas the 18-electron centers M' bear a residual negative charge,<sup>3d,e,4</sup> delocalized within the metal-ligand fragment, according to M'<sup>δ-</sup>-ML<sub>2</sub><sup>2δ+</sup>-M'<sup>δ-</sup>. This polarity can lead to selective reactivity patterns, as shown by the hydrogenation of terminal acetylenes with *trans*-Pt[Mo(CO)<sub>3</sub>Cp]<sub>2</sub>(C<sub>6</sub>H<sub>11</sub>NC)<sub>2</sub> as catalyst.<sup>8</sup>

(iii) They are well-suited for spectroscopic studies since linear trimetallic systems generally give rise to a sharp and intense far-infrared absorption, assignable to the ν<sub>as</sub>(M-M') vibration.<sup>3c,9-13</sup> The determination of the corresponding force constants<sup>13-16</sup> is a valuable means for studying the influence of electronic factors on metal-metal bond strength.<sup>17,18</sup>

With this in mind, we envisaged to extend the class of linear trimetallic complexes to a new series where the central metal in the chain would be gold, as in the anions [M'-Au-M']<sup>-</sup>. Indeed, it was anticipated that Au(I) would adopt here its preferred linear coordination, similar to that of Hg(II) in the well-known<sup>19</sup> isoelectronic M'-Hg-M' complexes. As a result, it was expected that interesting comparisons could perhaps be made between trimetallic chains differing from each other only by the nature of the central ion, its oxidation number [Hg(II) vs. Au(I)], or its coordination number [CN = 4 for Pt(II) and Pd(II); CN = 2 for Hg(II) and Au(I)]. Furthermore, at the

time we began this research, there was no example of a linear, symmetric gold(I)-transition metal complex, the only known molecules containing a gold-transition metal bond being of the bimetallic type, e.g. L → Au-M'<sup>20-22</sup> or of the osmium-gold cluster type.<sup>23a</sup> In the mean time, many gold-containing mixed-metal clusters have been reported.<sup>23b</sup>

Herein, we present our results on the desired [M'-Au-M']<sup>-</sup> complexes, the X-ray structure determination of [*n*-Bu<sub>4</sub>N][Au[Cr(CO)<sub>3</sub>Cp]<sub>2</sub>] and <sup>197</sup>Au Mössbauer data.<sup>17</sup> The synthesis of some of these complexes has appeared in a preliminary note.<sup>18</sup>

## Results and Discussion

In order to prepare the trimetallic [M'-Au-M']<sup>-</sup> complexes, we first developed a convenient synthesis of what seemed to us their most likely and logical precursors, i.e. the dihaloaurate(I) anions [X-Au-X]<sup>-</sup> (X = Cl, Br, I).<sup>24</sup> The tetraethyl- or tetra-*n*-butylammonium salts of the latter were then reacted in tetrahydrofuran (THF) with 2 equiv of sodium carbonylmetalates, NaM', and afforded indeed the desired complexes [R<sub>4</sub>N][M'-Au-M'] (1-6; eq 2).<sup>17</sup>



- 1: R = Et, M' = Mn(CO)<sub>5</sub>
- 2: R = Et, M' = Co(CO)<sub>4</sub>
- 3: R = *n*-Bu, M' = Cr(CO)<sub>3</sub>Cp
- 4: R = Et, M' = Mo(CO)<sub>3</sub>Cp
- 5: R = *n*-Bu, M' = W(CO)<sub>3</sub>Cp
- 6: R = *n*-Bu, M' = Fe(CO)<sub>2</sub>Cp

The reactions were monitored by infrared spectroscopy in the ν(CO) region. They were usually performed at low temperature (to avoid product decomposition) where rapid replacement of the halides by the carbonylmetalates took place, with formation of the metal-metal bonds. Details are given in the Experimental Section. Often, a typical difficulty with gold(I) complexes is their ease of dismutation or reduction, with formation of metallic gold. Thus, it turned out that the synthesis of **2** was difficult to perform from [Et<sub>4</sub>N][AuCl<sub>2</sub>], variable yields being obtained because of partial decomposition into metallic gold (blue-violet colloidal suspension or gold mirror). This was circumvented by using [Et<sub>4</sub>N][AuBr<sub>2</sub>] as precursor: the latter is less easily reduced than the corresponding chloride, and this favors the halide substitution over the electron-transfer mechanism.<sup>18</sup> Thus, the reduction potential of AuBr<sub>2</sub><sup>-</sup> is -0.55 V whereas for AuCl<sub>2</sub><sup>-</sup> it is -0.25 V (vs. SCE in propylene carbonate + TEAP/Pt electrode).<sup>25</sup> In general, we observed that the use of AuBr<sub>2</sub><sup>-</sup> instead of AuCl<sub>2</sub><sup>-</sup> would stabilize the reaction intermediate and that a larger cation (*n*-Bu<sub>4</sub>N vs. Et<sub>4</sub>N) would stabilize the reaction product. Thus, despite the high nucleophilicity and reducing properties of the anion [CpFe(CO)<sub>2</sub>]<sup>-</sup>, the use of [*n*-Bu<sub>4</sub>N][AuBr<sub>2</sub>] allowed their reaction to be carried out at room temperature, affording **6** in 81% yield. However, this complex in KBr pellets slowly decomposes in the infrared beam, *cis*-[CpFe(CO)<sub>2</sub>]<sub>2</sub> being progressively formed and spectroscopically characterized.<sup>26</sup> The bulky cation (Ph<sub>3</sub>PNPPH<sub>3</sub>)<sup>+</sup> has also been shown recently to confer a higher stability to the [Au[Co(CO)<sub>4</sub>]<sub>2</sub>]<sup>-</sup>

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anion.<sup>18,27</sup> Complexes 1–6 are best stored under nitrogen, in the dark, at low temperature.

**A. Infrared Spectroscopy.** The infrared spectra of complexes 1–6 are particularly informative in the regions of both carbonyl and metal–metal stretching vibrations: ca. 1800–2000 and 150–200  $\text{cm}^{-1}$ , respectively.

**Carbonyl Stretching Region.** Complex 1 exhibits three  $\nu(\text{CO})$  vibrations in THF between 2029 and 1920  $\text{cm}^{-1}$ , in agreement with the pattern expected for the terminal carbonyls of  $\text{Mn}(\text{CO})_5$  moieties.<sup>28</sup> As for  $\text{Mn}_2(\text{CO})_{10}$  or  $\text{Hg}[\text{Mn}(\text{CO})_5]_2$ , a staggered  $D_{4d}$  or eclipsed  $D_{4h}$  structure for 1 cannot be differentiated solely on the basis of IR data since three IR-active modes are expected in each case ( $2b_2 + e_1$  and  $2a_{2u} + e_u$ , respectively). Raman data are not available on our  $[\text{M}'\text{-Au-M}']^-$  complexes since they all decomposed in the laser beam of the spectrometer. Whereas  $\text{Mn}_2(\text{CO})_{10}$  has  $D_{4d}$  symmetry,<sup>29</sup> that of  $\text{Hg}[\text{Mn}(\text{CO})_5]_2$  is  $D_{4h}$ .<sup>30</sup> By analogy, 1, which is isoelectronic with the latter, could also have  $D_{4h}$  symmetry, like that recently found by X-ray diffraction for the related *trans*- $\text{Pt}[\text{Mn}(\text{CO})_5]_2(\text{CO})_2$ .<sup>31</sup> The three  $\nu(\text{CO})$  vibrations should therefore be assignable, in decreasing order, to the modes  $a_{2u}$ ,  $e_u$ , and  $a_{2u}$ . A definitive answer to this question should await the results of a crystal structure determination.

On the basis of its three  $\nu(\text{CO})$  vibrations between 2023 and 1929  $\text{cm}^{-1}$  and by analogy with the staggered structure of  $\text{Hg}[\text{Co}(\text{CO})_4]_2$ ,<sup>32</sup> we suggested for 2 a structure with  $D_{3d}$  symmetry (three IR-active  $\nu(\text{CO})$  modes:  $2a_{2u} + e_u$ ).<sup>17</sup> This has since been established by X-ray diffraction for the analogous  $[\text{Ph}_3\text{PNPPPh}_3][\text{Au}[\text{Co}(\text{CO})_4]_2]$ .<sup>27</sup> Noteworthy, a staggered conformation of the carbonyls was also found earlier in the linear trimetallic *trans*- $\text{Pt}[\text{Co}(\text{CO})_4]_2(\text{py})_2$ .<sup>33</sup>

The  $\nu(\text{CO})$  pattern of a complex in which two cyclopentadienylmetal tricarbonyl groups are *trans* with respect to each other is usually not sufficient to identify the symmetry of the molecule.<sup>34,5</sup> Based on IR data, the solid-state structure of  $\text{Hg}[\text{Mo}(\text{CO})_3\text{Cp}]_2$  was expected to be of  $C_{2h}$ <sup>10</sup> or of  $C_2$  symmetry.<sup>34,35</sup> The second hypothesis has since been confirmed by X-ray diffraction.<sup>36</sup> On the other hand, the predicted  $C_2$  symmetry<sup>35</sup> for  $\text{Zn}[\text{Mo}(\text{CO})_3\text{Cp}]_2$  was not confirmed, the latter having a *trans*  $C_{2h}$  structure in the solid.<sup>37</sup> For the chromium, molybdenum, and tungsten complexes (3–5), four, two, or three  $\nu(\text{CO})$  absorptions, respectively, are observed in their solid-state spectrum, whereas three  $\nu(\text{CO})$  bands are found in THF for all three compounds. In the isoelectronic mercury complexes  $\text{M}'\text{-Hg-M}'$ , a simplification of the infrared  $\nu(\text{CO})$  pattern is often observed on going from the solid to the solution spectrum.<sup>34,35</sup> Three  $\nu(\text{CO})$  modes are expected for a *trans*  $C_{2h}$  structure ( $a_u + 2b_u$ ), but accidental partial overlap of the more numerous absorptions due to the *cis*  $C_{2v}$  isomer ( $2a_1 + 2b_2 + b_1$ ) or to the *gauche*  $C_2$  isomer ( $3a + 3b$ ) could also occur and reduce the number of bands. Furthermore, solution- and solid-state structures need not be

Scheme I

| central metal in the chain | Pd | Pt | Au | Hg |
|----------------------------|----|----|----|----|
| coordination number        | 4  | 4  | 2  | 2  |
| oxidation state            | II | II | I  | II |

identical, and different rotamers could be present in solution, as demonstrated for  $[\text{CpMo}(\text{CO})_3]_2$ .<sup>38</sup> The solid-state structure of 3 has been determined by X-ray diffraction (see below) and reveals  $C_2$  symmetry for the complex anion. It is reasonable to assume similar structures for 4 and 5. Finally, three  $\nu(\text{CO})$  vibrations are observed for 6 in the solid and in solution, between 1912–1840 and 1923–1871  $\text{cm}^{-1}$ , respectively. This would be consistent with a *cis*  $C_{2v}$  symmetry of the trimetallic anion (IR-active  $\nu(\text{CO})$  modes:  $a_1 + b_1 + b_2$ ). Noteworthy, a similar structure has been postulated for the isoelectronic  $\text{Hg}[\text{Fe}(\text{CO})_2\text{Cp}]_2$ .<sup>39</sup>

In general for complexes 1–6, the  $\nu(\text{CO})$  frequencies are at higher energies relative to those of the corresponding sodium carbonylmetalates. This is indicative of an electron transfer from  $[\text{M}']^-$  to the Au(I) center, decreasing the electron density on the metal–carbonyl fragment, when compared with  $\text{Na}[\text{M}']$ . On the other hand, the  $\nu(\text{CO})$  frequencies of the  $[\text{M}'\text{-Au-M}']^-$  anions are at lower energies than those for the corresponding  $\text{Ph}_3\text{P}\rightarrow\text{Au-M}'$  complexes,<sup>20–22</sup> establishing that  $[\text{M}']^-$  is a better donor than  $\text{PPh}_3$ . As seen in Table I, the average  $\bar{\nu}(\text{CO})$  frequency<sup>3d,e,4</sup> of 1–6 is intermediate between that of the  $[\text{M}']^-$  anion and of the corresponding neutral dimer  $\text{M}'\text{-M}'$ . This illustrates the anionic character retained by the  $\text{M}'$  fragments in the  $[\text{M}'\text{-Au-M}']^-$  complexes. In comparison, the corresponding values for the  $\text{M}'\text{-Hg-M}'$  complexes, closer to those of the  $\text{M}'\text{-M}'$  dimers, show that these complexes have a more covalent character than their gold analogues, as confirmed below by the study of their metal–metal bond strengths. For each metal carbonyl group  $\text{M}'$  of Table I, the average  $\bar{\nu}(\text{CO})$  frequency increases in the sequence  $[\text{M}']^- < \text{M}'\text{-Pd}(\text{py})_2\text{-M}' < [\text{M}'\text{-Pt}(\text{py})_2\text{-M}'] < [\text{M}'\text{-Au-M}']^- < \text{M}'\text{-Hg-M}' < \text{M}'\text{-M}'$ . This order parallels an increasing covalency for these molecules or, in other words, a decreasing residual charge  $|\delta|$  on  $\text{M}'$ , ranging formally from 1– for the carbonylmetalates to 0 for the dimers.

**Metal–Metal Stretching Region.** Complexes with a linear trimetallic skeleton are found to usually give rise to a strong absorption band in the far-infrared region, assigned predominantly to the asymmetric metal–metal stretching mode.<sup>3c,9,10</sup> Its detection is of importance on two accounts. First, it is a means of establishing the presence of such bonding in the corresponding molecules, and second, it allows the determination of force constants for these systems. The only important feature observed between 100 and 300  $\text{cm}^{-1}$  in the FT far-infrared spectrum of complexes 1–6 is indeed a strong and sharp absorption, found between 170 and 200  $\text{cm}^{-1}$ . As a result, the mixing of the  $\nu_{as}(\text{Au-M}')$  mode with others of same symmetry can reasonably be assumed to be minimal. The metal–metal frequencies are reported in Table I and compared with the values for the corresponding  $\text{M}'\text{-Hg-M}'$ ,  $\text{M}'\text{-Pd}(\text{py})_2\text{-M}'$ , and  $\text{M}'\text{-Pt}(\text{py})_2\text{-M}'$  complexes. The approximate<sup>16</sup> force constants  $k - k_{12}$  allow a comparison between these systems and an evaluation, at  $\text{M}'$  constant, of the influence of a change in the oxidation state or in the coordination number of the central ion when one of these two factors is varied, the other one remaining unchanged.

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Table I. Selected Spectroscopic and Structural Data in Linear Trimetallic and Related Complexes

| compd   | M'-M-M'<br>bond | $\bar{\nu}(\text{CO})_2^a$<br>cm <sup>-1</sup> | $-\delta, ^b e$   | ref       | $\nu_{\text{as}}^-$<br>(M-M'), <sup>c</sup><br>cm <sup>-1</sup> | $k-k_{12}^-$<br>(M-M'), <sup>d</sup><br>mdyn Å <sup>-1</sup> | $d(\text{M-M}')$ , Å   | ref           |
|---|-----------------|--|-------------------|-----------|---|--|------------------------|---------------|
| Na[Mn(CO) <sub>5</sub> ]  |                 | 1863 <sup>e</sup>                              | 1                 | 3d        |   |  |                        |               |
| <i>trans</i> -Pd[Mn(CO) <sub>5</sub> ] <sub>2</sub> (py) <sub>2</sub>                 | Mn-Pd-Mn        | 1949 <sup>e</sup>                              | 0.45              | 3d        | 149 s   | 0.35   |                        | 3c            |
| <i>trans</i> -Pt[Mn(CO) <sub>5</sub> ] <sub>2</sub> (py) <sub>2</sub>                 | Mn-Pt-Mn        | 1951 <sup>e</sup>                              | 0.42              | 3d        | 155 s   | 0.50   | 2.743                  | 3c, 33        |
| 1   | Mn-Au-Mn        | 1962 <sup>e</sup>                              | 0.35              | this work | 185 s   | 0.71   |                        | 18, this work |
| Ph <sub>3</sub> P→Au-Mn(CO) <sub>5</sub>  | Mn-Au           | 1994 <sup>h</sup>                              | 0.15              | 20, 21    |   |  | 2.52 ± 0.03            | 51            |
| Hg[Mn(CO) <sub>5</sub> ] <sub>2</sub>   | Mn-Hg-Mn        | 2010 <sup>f,k</sup>                            | 0.10              | 19a, 41   | 188   | 0.74   | 2.610 (2)              | 9, 10, 30, 41 |
| Mn <sub>2</sub> (CO) <sub>10</sub>  | Mn-Mn           | 2017 <sup>i</sup>                              | 0                 | 42        |   |  |                        |               |
| Na[Co(CO) <sub>4</sub> ]  |                 | 1885 <sup>e</sup>                              | 1                 | 3e        |   |  |                        |               |
| <i>trans</i> -Pd[Co(CO) <sub>4</sub> ] <sub>2</sub> (py) <sub>2</sub>                 | Co-Pd-Co        | 1958 <sup>e</sup>                              | 0.55              | 3e        | 168 s   | 0.46   |                        | 3c            |
| <i>trans</i> -Pt[Co(CO) <sub>4</sub> ] <sub>2</sub> (py) <sub>2</sub>                 | Co-Pt-Co        | 1949 <sup>e</sup>                              | 0.60              | 3e        | 177 s   | 0.68   | 2.613                  | 3c, 33        |
| 2   | Co-Au-Co        | 1957 <sup>f</sup>                              | 0.55              | this work | 189 s   | 0.77   | 2.509 (2) <sup>o</sup> | 18, this work |
| Ph <sub>3</sub> P→Au-Co(CO) <sub>4</sub>  | Co-Au           | 1989 <sup>l</sup>                              | 0.35              | 20        |   |  | 2.50 (1)               | 49            |
| Hg[Co(CO) <sub>4</sub> ] <sub>2</sub>   | Co-Hg-Co        | 2027 <sup>h,j</sup>                            | 0.10              | 43        | 197   | 0.85   |                        | 9, 10         |
| Co <sub>2</sub> (CO) <sub>8</sub>   | Co-Co           | 2044 <sup>j</sup>                              | 0                 | 44        |   |  |                        |               |
| Na[Cr(CO) <sub>3</sub> Cp]  |                 | 1812 <sup>e</sup>                              | 1                 | 6a        |   |  |                        |               |
| <i>trans</i> -Pt[Cr(CO) <sub>3</sub> Cp] <sub>2</sub> ( <i>t</i> -BuNC) <sub>2</sub>  | Cr-Pt-Cr        | 1858 <sup>f</sup>                              | 0.60              | 6b        | 174 s   | 0.60   |                        | 6b            |
| 3   | Cr-Au-Cr        | 1886 <sup>e</sup>                              | 0.35              | this work | 194 s   | 0.75   | 2.64                   | this work     |
| Ph <sub>3</sub> P→Au-Cr(CO) <sub>3</sub> Cp   | Cr-Au           | 1883 <sup>i</sup>                              | 0.35              | 22        |   |  |                        |               |
| Hg[Cr(CO) <sub>3</sub> Cp] <sub>2</sub>   | Cr-Hg-Cr        | 1935 <sup>j</sup>                              | -0.05             | 34        | 186   | 0.70   |                        | 9             |
| [Cr(CO) <sub>3</sub> Cp] <sub>2</sub>   | Cr-Cr           | 1928 <sup>j</sup>                              | 0                 | 34        |   |  |                        |               |
| Na[Mo(CO) <sub>3</sub> Cp]  |                 | 1812 <sup>e</sup>                              | 1                 | 3e        |   |  |                        |               |
| <i>trans</i> -Pd[Mo(CO) <sub>3</sub> Cp] <sub>2</sub> (py) <sub>2</sub>               | Mo-Pd-Mo        | 1842 <sup>f</sup>                              | 0.80 <sup>m</sup> | 3e        | 134 s   | 0.36   |                        | 3c            |
| <i>trans</i> -Pt[Mo(CO) <sub>3</sub> Cp] <sub>2</sub> (py) <sub>2</sub>               | Mo-Pt-Mo        | 1835 <sup>f</sup>                              | 0.85 <sup>m</sup> | 3e, 4     | 144 w   | 0.59   |                        | 3c            |
| 4   | Mo-Au-Mo        | 1894 <sup>e</sup>                              | 0.45              | this work | 170 s   | 0.83   |                        | 18, this work |
| Ph <sub>3</sub> P→Au-Mo(CO) <sub>3</sub> Cp   | Mo-Au           | 1893 <sup>i</sup>                              | 0.45              | 22        |   |  |                        |               |
| Hg[Mo(CO) <sub>3</sub> Cp] <sub>2</sub>   | Mo-Hg-Mo        | 1951 <sup>g</sup>                              | 0.10              | 10        | 178   | 0.91   | 2.746 (2)              | 9, 36         |
| [Mo(CO) <sub>3</sub> Cp] <sub>2</sub>   | Mo-Mo           | 1962 <sup>e</sup>                              | 0                 | 3e        |   |  |                        |               |
| NaW(CO) <sub>3</sub> Cp   |                 | 1811 <sup>e</sup>                              | 1                 | 6a, 45    |   |  |                        |               |
| <i>trans</i> -Pt[W(CO) <sub>3</sub> Cp] <sub>2</sub> ( <i>ter</i> -BuNC) <sub>2</sub> | W-Pt-W          | 1877 <sup>f</sup>                              | 0.50              | 4         | 141 m   | 0.75   |                        | 4             |
| 5   | W-Au-W          | 1886 <sup>e</sup>                              | 0.50              | this work | 152 s   | 0.87   |                        | this work     |
| Ph <sub>3</sub> P→Au-W(CO) <sub>3</sub> Cp  | W-Au            | 1888 <sup>i</sup>                              | 0.50              | 22        |   |  | 2.698 (3)              | 48            |
| Hg[W(CO) <sub>3</sub> Cp] <sub>2</sub>  | W-Hg-W          | 1945 <sup>g</sup>                              | 0.05              | 10        | 166   | 1.05   |                        | 9             |
| [W(CO) <sub>3</sub> Cp] <sub>2</sub>  | W-W             | 1956 <sup>e</sup>                              | 0                 | this work |   |  |                        |               |
| NaFe(CO) <sub>2</sub> Cp  |                 | 1842 <sup>e</sup>                              | <i>n</i>          | 17        |   |  |                        |               |
| 6   | Fe-Au-Fe        | 1900 <sup>e</sup>                              | <i>n</i>          | this work | 193 s   | 0.78   |                        | 18, this work |
| Hg[Fe(CO) <sub>2</sub> Cp] <sub>2</sub>   | Fe-Hg-Fe        | 1958 <sup>g</sup>                              | <i>n</i>          | 46        | 200   | 0.84   |                        | 9             |

<sup>a</sup> The calculation of the average  $\bar{\nu}(\text{CO})$  frequency takes into account the dimensions of the irreducible representations, as indicated in: Kahn, O.; Bigorgne, M. *J. Organomet. Chem.* **1967**, *10*, 137. <sup>b</sup> The definition of the residual negative charge  $\delta$  on the M' fragment is given in the text; considering that all the  $\nu(\text{CO})$  frequencies are not measured under the same conditions, the value of  $\delta$  has been rounded off to the nearest 0.05 e. <sup>c</sup> The frequencies are given for solid samples. <sup>d</sup> Only the difference  $k - k_{12}$  ( $k_{12}$  = stretch-stretch interaction constant) can be obtained from  $\nu_{\text{as}}$  values, and we could not assign the bending mode  $\delta(\text{M}'\text{-M-M}')$ . <sup>e</sup> From values in THF. <sup>f</sup> From values in KBr. <sup>g</sup> From values in CHCl<sub>3</sub>. <sup>h</sup> From values in CCl<sub>4</sub>. <sup>i</sup> From values in hexane. <sup>j</sup> From values in *n*-heptane. <sup>k</sup> From values in the solid. <sup>l</sup> From values in CS<sub>2</sub>. <sup>m</sup> This value is somewhat higher than that originally reported in ref 3e (0.55 e) because the  $\bar{\nu}(\text{CO})$  value has been recalculated, considering only the three most significant absorptions of the complex, as in ref 4. <sup>n</sup> The  $\delta$  value cannot be calculated since the necessary  $\nu(\text{CO})$  data for the unbridged form of [Fe(CO)<sub>2</sub>Cp]<sub>2</sub> are not available. <sup>o</sup> This value is for the (PPN)<sup>+</sup> salt of the complex.<sup>27</sup>

We observe an increase in metal-metal bond strength in the M'-M-M' systems in the following sequence of M = Pd < Pt < Au < Hg. The same trend was found above for the covalency of the complexes when the vibrations of the CO ligands were observed and is now also deduced from the metal-metal vibrations. In all cases, a higher covalency of these molecules, as reflected by the higher average  $\bar{\nu}(\text{CO})$  frequencies, parallels stronger metal-metal bonds, as evidenced by their force constants.

The correlation previously established concerning the influence of electronic factors on metal-metal force constants in linear trimetallic systems<sup>18</sup> M'-M-M' is now also verified when M' = Cr(CO)<sub>3</sub>Cp and can be summarized as follows: (i) An increase in the oxidation state of the central ion in the chain is accompanied by an increase of the metal-metal bond strength (Scheme Ia). (ii) An increase in the coordination number of the central ion results in a decreased metal-metal bond strength (Scheme Ib).

For comparison, we have measured the  $\nu_{\text{as}}(\text{Cu-Co})$  frequency in [Et<sub>4</sub>N][Cu[Co(CO)<sub>4</sub>]<sub>2</sub>].<sup>40</sup> The value of 245 cm<sup>-1</sup>,

corresponding to a force constant of 0.73 mdyn Å<sup>-1</sup> is, as expected, indicative of the Cu-Co bond being weaker than the Au-Co bond in **2**. This parallels the well-established trend that metal-metal bond strength increases when going from the first- to the third-row metals.

### B. Molecular Structure of [*n*-Bu<sub>4</sub>N][Au[Cr(CO)<sub>3</sub>Cp]<sub>2</sub>] (3).

In the crystalline state, isolated Au[Cr(CO)<sub>3</sub>Cp]<sub>2</sub><sup>-</sup> anions of **3** with approximate C<sub>2</sub> symmetry are found. The noncrystallographic axis of rotation passes through the gold atom and the midpoint between C(3) and C(4) (Figure 1; Tables II and III). C(3) and C(4) are coplanar with the three metal atoms

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**Table II.** Final Fractional Atomic Coordinates with Esd's in Parentheses for  $[n\text{-Bu}_4\text{N}][\text{Au}[\text{Cr}(\text{CO})_3\text{Cp}]_2]$  (3)

| atom <sup>a</sup> | x/a        | y/b        | z/c        | B, Å <sup>2</sup> | atom  | x/a        | y/b        | z/c        | B, Å <sup>2</sup> |
|-------------------|------------|------------|------------|-------------------|-------|------------|------------|------------|-------------------|
| Au                | 0.1116 (3) | 0.1783 (2) | 0.2722 (1) |                   | Cr(2) | 0.0509 (9) | 0.1484 (5) | 0.1417 (4) |                   |
| Cr(1)             | 0.1195 (9) | 0.2458 (5) | 0.3821 (4) |                   | C(4)  | 0.138 (5)  | 0.071 (3)  | 0.209 (3)  | 6.1 (14)          |
| C(1)              | -0.052 (6) | 0.208 (3)  | 0.313 (3)  | 6.2 (15)          | O(4)  | 0.196 (4)  | 0.009 (2)  | 0.242 (2)  | 8.8 (11)          |
| O(1)              | -0.163 (5) | 0.168 (3)  | 0.278 (2)  | 10.7 (12)         | C(5)  | 0.157 (6)  | 0.242 (4)  | 0.178 (3)  | 7.5 (17)          |
| C(2)              | 0.083 (5)  | 0.195 (3)  | 0.441 (2)  | 5.3 (12)          | O(5)  | 0.208 (4)  | 0.306 (3)  | 0.196 (2)  | 11.4 (13)         |
| O(2)              | 0.062 (3)  | 0.160 (2)  | 0.480 (2)  | 5.9 (8)           | C(6)  | 0.188 (9)  | 0.130 (5)  | 0.119 (4)  | 12.2 (25)         |
| C(3)              | 0.263 (6)  | 0.165 (3)  | 0.408 (2)  | 5.1 (12)          | O(6)  | 0.288 (7)  | 0.110 (4)  | 0.118 (3)  | 19.0 (25)         |
| O(3)              | 0.360 (4)  | 0.126 (2)  | 0.431 (2)  | 7.8 (11)          | C(10) | 0.900 (7)  | 0.175 (5)  | 0.032 (3)  | 11.0 (19)         |
| C(15)             | 0.044 (8)  | 0.362 (4)  | 0.396 (4)  | 9.9 (20)          | C(11) | 0.860 (7)  | 0.205 (4)  | 0.074 (3)  | 9.7 (19)          |
| C(16)             | 0.045 (6)  | 0.366 (3)  | 0.336 (3)  | 7.3 (15)          | C(12) | 0.823 (6)  | 0.149 (4)  | 0.110 (3)  | 8.2 (17)          |
| C(17)             | 0.198 (6)  | 0.351 (3)  | 0.357 (3)  | 7.6 (16)          | C(13) | 0.859 (6)  | 0.079 (4)  | 0.085 (3)  | 9.3 (18)          |
| C(18)             | 0.275 (7)  | 0.348 (4)  | 0.422 (3)  | 9.5 (19)          | C(14) | 0.884 (6)  | 0.096 (4)  | 0.038 (3)  | 9.0 (18)          |
| C(19)             | 0.184 (7)  | 0.352 (3)  | 0.444 (3)  | 8.6 (17)          | N     | 0.364 (4)  | 0.533 (2)  | 0.132 (2)  | 5.3 (10)          |
| C(30)             | 0.314 (5)  | 0.520 (3)  | 0.180 (3)  | 5.4 (13)          | C(40) | 0.228 (5)  | 0.529 (3)  | 0.054 (2)  | 5.0 (12)          |
| C(31)             | 0.422 (5)  | 0.525 (3)  | 0.257 (2)  | 5.1 (13)          | C(41) | 0.234 (6)  | 0.541 (3)  | -0.011 (3) | 6.3 (14)          |
| C(32)             | 0.351 (6)  | 0.495 (4)  | 0.303 (3)  | 8.6 (17)          | C(42) | 0.100 (6)  | 0.545 (3)  | -0.081 (3) | 8.4 (17)          |
| C(33)             | 0.459 (6)  | 0.510 (4)  | 0.383 (3)  | 9.2 (18)          | C(43) | 0.102 (5)  | 0.558 (3)  | -0.143 (3) | 6.2 (13)          |
| C(50)             | 0.440 (6)  | 0.613 (3)  | 0.142 (3)  | 6.6 (15)          | C(60) | 0.477 (6)  | 0.474 (3)  | 0.137 (3)  | 6.9 (15)          |
| C(51)             | 0.342 (5)  | 0.683 (4)  | 0.139 (2)  | 5.8 (12)          | C(61) | 0.427 (6)  | 0.391 (4)  | 0.123 (3)  | 8.8 (17)          |
| C(52)             | 0.432 (7)  | 0.754 (4)  | 0.156 (3)  | 8.6 (17)          | C(62) | 0.546 (7)  | 0.330 (5)  | 0.132 (3)  | 11.7 (21)         |
| C(53)             | 0.371 (7)  | 0.818 (5)  | 0.166 (3)  | 13.4 (23)         | C(63) | 0.523 (12) | 0.253 (7)  | 0.125 (6)  | 23.4 (44)         |

<sup>a</sup> The *n*-butyl groups of  $\text{NBu}_4^+$  are numbered C(30)–C(34), C(40)–C(44), C(50)–C(54), and C(60)–C(64).

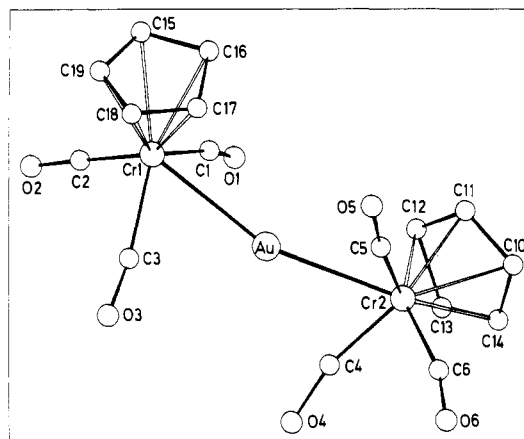
**Table III.** Distances (pm) and Angles (deg)

|                            |           |                            |          |
|----------------------------|-----------|----------------------------|----------|
| Au–Cr(1)                   | 264.1 (9) | Cr(1)–M(1) <sup>a</sup>    | 188      |
| Au–Cr(2)                   | 263.5 (8) | Cr(2)–C(4)                 | 182 (5)  |
| Cr(1)–C(1)                 | 180 (6)   | Cr(2)–C(5)                 | 187 (7)  |
| Cr(1)–C(2)                 | 178 (5)   | Cr(2)–C(6)                 | 187 (11) |
| Cr(1)–C(3)                 | 194 (6)   | Cr(2)–M(2) <sup>a</sup>    | 182      |
| Cr(1)–Au–Cr(2)             | 162.2 (3) | Au–Cr(2)–M(2) <sup>a</sup> | 119.8    |
| Au–Cr(1)–M(1) <sup>a</sup> | 116.1     | Au–Cr(2)–C(4)              | 62 (2)   |
| Au–Cr(1)–C(1)              | 64 (2)    | Au–Cr(2)–C(5)              | 68 (2)   |
| Au–Cr(1)–C(2)              | 123 (2)   | Au–Cr(2)–C(6)              | 124 (3)  |
| Au–Cr(1)–C(3)              | 65 (2)    | C(4)–Cr(2)–C(5)            | 108 (3)  |
| C(1)–Cr(1)–C(2)            | 84 (3)    | C(4)–Cr(2)–C(6)            | 89 (3)   |
| C(2)–Cr(1)–C(3)            | 85 (2)    | C(5)–Cr(2)–C(6)            | 81 (3)   |
| C(1)–Cr(1)–C(3)            | 109 (3)   |                            |          |

<sup>a</sup> M represents the centers of the Cp rings.

and cis relative to the Cr(1)–Au–Cr(2) axis. This is an unusual aspect of this structure. The Cr(1)–Au–Cr(2) bond angle of 162.2 (3)°, which is rather small (but not exceptional) for two-coordinate Au(I), probably results from this particular steric situation.

The coordination of the chromium atoms is of the "four-legged piano-stool",  $\text{CpM}(\text{CO})_3\text{L}$ , type.<sup>47</sup> While the angles between the mutually trans CO ligands C(1)–Cr(1)–C(3) (109 (3)°) and C(4)–Cr(2)–C(5) (108 (3)°) are typical for this geometry, the Au–Cr–C(CO) angles, particularly the Au–Cr–C(CO) cis angles (62 (2)–68 (2)°), are smaller than the usual L–M–C(CO) values. However, this is not an uncommon observation in complexes with metal–metal bonds: bond angles of the same magnitude have been found in  $\text{Cp}(\text{CO})_3\text{W–Au} \leftarrow \text{PPh}_3$ ,<sup>48</sup> which is geometrically comparable with 3. In  $(\text{CO})_4\text{Co–Au} \leftarrow \text{PPh}_3$ ,<sup>49</sup>  $\text{Au}[\text{Co}(\text{CO})_4]_2$ ,<sup>27</sup> and  $(\text{CO})_6\text{V–Au} \leftarrow \text{PPh}_3$ ,<sup>50</sup> CO ligands are also bent toward the gold atom, and in  $\text{M'–Hg–M'}$  complexes, similar distortions are observed.<sup>36,53–55</sup>

**Figure 1.** Structure of the anion  $\text{Au}[\text{Cr}(\text{CO})_3\text{Cp}]_2^-$  (3) with the numbering scheme.

The acute Au–Cr–C(CO) cis angles are also reflected in the Au...C(CO) contacts. These involve C(4), C(1), C(3), and C(5) and range in this order from 240 (6) to 261 (6) pm. Similar values have been found in other metal–metal–bonded gold(I) complexes<sup>48,50,52,56,57</sup> and are usually ascribed to steric reasons, rather than to significant bonding interactions between these ligands and gold.

In  $\text{M'–Au} \leftarrow \text{PPh}_3$  complexes,  $\text{M'}$  being a first-row transition-metal carbonyl moiety,  $\text{M'–Au}$  distances between 250 and 269 pm have been found.<sup>49–52</sup> The Au–Co distance in  $\text{Au}[\text{Co}(\text{CO})_4]_2^-$  is 250.9 (2) pm. In 3 the Au–Cr distances (264.1 (9) and 263.5 (8) pm) are at the upper border of this range but are shorter than the H-bridged Au–Cr distance in  $\text{AuCr}(\mu\text{-H})(\text{CO})_5\text{PPh}_3$  (277.0 (2) pm).<sup>58</sup> They are close to the Au–W bond lengths in  $\text{Cp}(\text{CO})_3\text{W–Au} \leftarrow \text{PPh}_3$  (269.8 (3) pm).<sup>48</sup> A series of related complexes with linear  $\text{M'–Hg–Co}$  units shows that the Hg–Co distance varies from about 250 pm in  $\text{Hg}[\text{Co}(\text{CO})_3\text{PET}_3]_2$ <sup>53</sup> and  $\text{Hg}[\text{Co}(\text{CO})_4]_2$ <sup>27</sup> to 256 pm in  $\text{Cp}(\text{CO})_2\text{FeHgCo}(\text{CO})_4$ <sup>54</sup> and 267.6 pm in  $\text{Hg}[\text{Co}(\text{P}(\text{OMe})_3)_4]_2$ .<sup>55</sup> Obviously, the metal–metal distances in linear

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Table IV. Gold-197 Mössbauer Data (4.2 K)<sup>a</sup>

| compd  | IS, <sup>b</sup> mm/s | QS, mm/s |
|--|-----------------------|----------|
| ( <i>n</i> -Bu <sub>4</sub> N)AuCl <sub>2</sub>                              | 0.31 (7)              | 5.93 (7) |
| ( <i>n</i> -Bu <sub>4</sub> N)AuI <sub>2</sub>                               | 0.30 (7)              | 5.61 (7) |
| [Et <sub>4</sub> N][Au[Mn(CO) <sub>5</sub> ] <sub>2</sub> ] (1)              | 1.23 (6)              | 5.60 (6) |
| [ <i>n</i> -Bu <sub>4</sub> N][Au[Fe(CO) <sub>5</sub> Cp] <sub>2</sub> ] (6) | 1.45 (8)              | 4.87 (8) |
| [Et <sub>4</sub> N][Au[Mo(CO) <sub>5</sub> Cp] <sub>2</sub> ] (4)            | 1.47 (5)              | 5.89 (5) |

<sup>a</sup> Fitting errors are given in parentheses. <sup>b</sup> Relative to <sup>197</sup>Au in Pt at 4.2 K.

M'-M-M' or L→M-M' complexes are easily influenced by steric and/or electronic effects of the ligands both at M and M'. Similar conclusions have been drawn from the structures of bridge-supported metal-metal bonds in binuclear complexes.<sup>59</sup>

**C. Gold-197 Mössbauer Parameters and the Nature of the Au-Metal Bond in the Linear Trimetallic Complexes.** Most gold compounds give doublet spectra in <sup>197</sup>Au Mössbauer spectroscopy.<sup>60</sup> Such spectra are characterized by the isomer shift, IS, and the quadrupole splitting, QS. The former parameter is a measure of the total electron density at the gold nucleus, and an increase in IS reflects principally an increase in the population of the valence shell 6s orbital of the gold atom. The QS is a measure of the asymmetry of distribution of electronic charge about the gold nucleus, i.e. the difference in population between the 6p<sub>z</sub> orbital and the 6p<sub>x</sub> and 6p<sub>y</sub> orbitals.

When our <sup>197</sup>Au Mössbauer results on the [AuX<sub>2</sub>]<sup>-</sup> (X = Cl, Br) and [AuM'<sub>2</sub>]<sup>-</sup> ions became available,<sup>17</sup> only few systematic studies on Au(I) complexes had been reported<sup>61,62</sup> and there was still some debate about the gold hybridization model in auroic complexes (sp<sub>z</sub> vs. d<sub>z<sup>2</sup></sub> s). The arguments in favor of the sp<sub>z</sub> hybridization model need no longer to be detailed<sup>17</sup> since, in the mean time, they have been discussed in the literature.<sup>63-65</sup> This model, rather than the earlier proposal involving d<sub>z<sup>2</sup></sub>s hybridization,<sup>66</sup> easily explains the experimental observations now available. Thus, it is found that in Au(I) complexes the isomer shift (s-orbital participation) and quadrupole splitting (p<sub>z</sub>-orbital participation) both increase as the ligands become better donors and the bonds more covalent. Particular interest for Au(I) symmetric linear complexes is justified by the fact that they allow comparisons between systems where the σ<sub>6s6p</sub> orbitals keep a constant contribution of the 6s and 6p atomic orbitals. Gold-197 IS and QS have been reported for such complexes including a great variety of donor ligands,<sup>60</sup> and the IS/QS linear relationship, which has been deduced from the experimental data, supports the hybrid σ<sub>6s6p</sub> model in these complexes.

The Mössbauer parameters reported here (Table IV) for the trimetallic linear Au(I) complexes supply useful information about the Au-metal bond. The IS's of the latter complexes are higher than those of the halide complexes and are close to those of a pseudohalogen complex.<sup>60</sup> This confirms the rather ionic nature of the Au-transition metal bond in these complexes. A typical spectrum is shown Figure 2. On the other hand, the QS values appear to be lower than the values

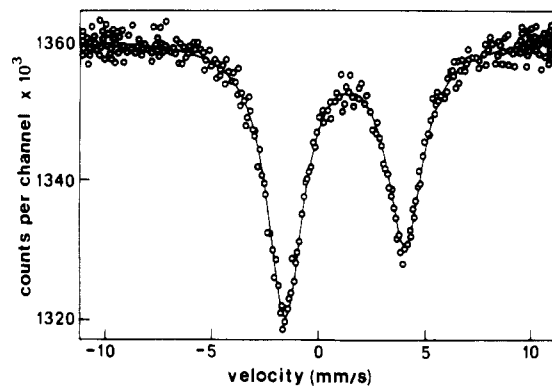
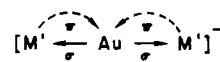


Figure 2. Gold-197 Mössbauer absorption spectrum of 1.

expected from IS/QS linear relationships.<sup>60,67</sup> This suggests a nonnegligible contribution to the electric field gradient of 6p<sub>x</sub> electrons, balancing partially the contribution of the 6p<sub>y</sub> electronic population involved in the σ<sub>6s6p</sub> hybrid orbital. The π contribution appears more pronounced in the Fe-Au-Fe complex (6) for which the QS value is the lowest found so far for a gold(I) molecular linear complex. Thus, the IS and QS of these trimetallic complexes are consistent with the following model already suggested by the IR study in which σ contributions largely dominate over π effects:



Such a bonding scheme<sup>68b</sup> was also found in the M[Fe(CO)<sub>2</sub>Cp]<sub>2</sub> (M = Zn, Cd, Hg) complexes by IR (ν(CO) region) and Fe Mössbauer studies:<sup>68a</sup>



This model would seem of general applicability for related systems, in particular for the AuI<sub>2</sub><sup>-</sup> complex. The low value of the QS in this complex compared with that of AuCl<sub>2</sub><sup>-</sup> (see Table IV and ref 60) suggests a greater π contribution in the former. Interestingly, it has been reported for AuCl<sub>2</sub><sup>-</sup> (a) that the ionic character of the Au-Cl bond is about 68% (from chlorine NQR frequencies), leaving a net charge of about +0.36 e on the Au atom,<sup>69</sup> and (b) that any π effect will arise from π donation into the gold 6p<sub>x</sub> and 6p<sub>y</sub> orbitals, Cl<sup>-</sup> being furthermore a weak ligand.<sup>70</sup>

These conclusions are in agreement with our own results.

### Experimental Section

All manipulations were carried out under an atmosphere of dry prepurified nitrogen. Tetrahydrofuran and diethyl ether were freshly distilled from a blue solution of sodium/benzophenone ketyl under nitrogen. Distilled water was degassed under nitrogen. The tetraalkylammonium dihaloaurates(I) [R<sub>4</sub>N][AuX<sub>2</sub>] were prepared as described in the literature.<sup>24</sup> The sodium carbonylmetalates were prepared by Na/Hg reduction of the corresponding binuclear complexes or by direct synthesis.<sup>6a</sup>

Elemental analyses of C, H, and N were performed by the Service Central de Microanalyses du CNRS.

Infrared spectra were recorded in the region 4000-400 cm<sup>-1</sup> on a Perkin-Elmer 398 spectrophotometer as KBr pellets (unless otherwise specified) and in the region 420-50 cm<sup>-1</sup> on a Polytec far-IR 30 FT interferometer as polythene disks.

**A. Syntheses. Tetraethylammonium Bis(pentacarbonylmanganio)aurate(I) (1).** To a stirred suspension of [Et<sub>4</sub>N][AuCl<sub>2</sub>]

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(1.00 g, 2.51 mmol) in THF (15 mL), placed in a dry ice/acetone bath, was added a filtered solution of  $\text{NaMn}(\text{CO})_5$  (5 mmol) in THF (20 mL) prepared from  $\text{Mn}_2(\text{CO})_{10}$  (0.97 g, 2.50 mmol). The solution became light orange. After 0.25 h of stirring at  $-60^\circ\text{C}$ , pentane (30 mL) was added, and the light beige precipitate that formed was filtered and dried. It was further washed with distilled water (to remove NaCl) and  $\text{Et}_2\text{O}$  and dried under vacuo, affording white microcrystals of pure **1**: yield 1.29 g, 1.80 mmol (72% based on Au); mp  $134^\circ\text{C}$ . IR<sup>71</sup> ( $\text{cm}^{-1}$ ):  $\nu(\text{CO})$  2023 s, 1950 s sh, 1909 vs;  $\nu(\text{CO})$  (THF) 2029 vs, 1949 vs, 1920 s; other bands, 3005 sh, 2995 w, 1481 s, 1456 m, 1439 m, 1414 w, 1388 m, 1362 m, 1186 w, 1170 ms, 1094 w, 1065 m, 1051 w, 1000 s, 783 s, 655 vs br, 487 m, 455 sh, 420 m;  $\nu_{\text{as}}(\text{AuMn})$  185 s; 124 mw. Anal. Calcd for  $\text{C}_{18}\text{H}_{20}\text{AuNO}_{10}\text{Mn}_2$  ( $M_r = 717.21$ ): C, 30.14; H, 2.81; N, 1.95. Found: C, 30.0; H, 2.75; N, 1.9.

**Tetraethylammonium Bis(tetracarbonylcobalto)aurate(I) (2)**. To a stirred suspension of  $[\text{Et}_4\text{N}][\text{AuBr}_2]$  (0.50 g, 1.03 mmol) in THF (10 mL), placed in a dry ice/acetone bath, was added a filtered solution of  $\text{NaCo}(\text{CO})_4$  (2.05 mmol) in THF (15 mL) prepared from  $\text{Co}_2(\text{CO})_8$  (0.35 g, 1.03 mmol). After 0.5 h of stirring at  $-60^\circ\text{C}$ , the light green solution was filtered and cold pentane (100 mL) added to it, causing the precipitation of a light gray powder. The solid was decanted while maintained at  $-60^\circ\text{C}$  and the supernatant solution removed. The powder was then washed twice with pentane, distilled water, and pentane again and dried under vacuo, affording pale cream **2**: yield 0.37 g, 0.55 mmol (54% based on Au); mp not measured, dec. IR<sup>71</sup> ( $\text{cm}^{-1}$ ):  $\nu(\text{CO})$  2023 vs, 1947 vs, 1929 sh; other bands, 1460 ms, 1395 w, 1177 m, 1027 w, 1002 w, 787 m, 562 s, 551 sh, 538 vs, 490 s, 461 sh, 432 m, 357 m, 227 w;  $\nu_{\text{as}}(\text{AuCo})$  189 s. Anal. Calcd for  $\text{C}_{16}\text{H}_{20}\text{AuCo}_2\text{NO}_8$  ( $M_r = 669.17$ ): C, 28.72; H, 3.01; N, 2.09. Found: C, 27.9; H, 3.0; N, 2.0.

**Tetra-*n*-butylammonium Bis(tricarbonyl( $\eta$ -cyclopentadienyl)chromio)aurate(I) (3)**. To a stirred suspension of  $[\text{n-Bu}_4\text{N}][\text{AuBr}_2]$  (0.60 g, 1.0 mmol) in THF (15 mL) was added at  $-40^\circ\text{C}$  a filtered solution of  $\text{Na}[\text{Cr}(\text{CO})_3\text{Cp}]$  (2.0 mmol) in THF (40 mL) prepared from  $[\text{Cr}(\text{CO})_3\text{Cp}]_2$  (0.40 g, 1.0 mmol). After 0.5-h stirring at  $-40^\circ\text{C}$ , the light yellow-green solution was stirred for 1 h at room temperature and then filtered. Pentane was added to the filtrate, and light yellow-green crystals of **3** formed after 24 h at  $-20^\circ\text{C}$ . They were collected, washed with pentane, and dried under vacuo. Single crystals suitable for X-ray diffraction were obtained from  $\text{CH}_2\text{Cl}_2$ /pentane: yield 0.55 g, 0.65 mmol (65% based on Au); mp  $124^\circ\text{C}$ . IR<sup>71</sup> ( $\text{cm}^{-1}$ ):  $\nu(\text{CO})$  1919 s, 1890 vs, 1825 m sh, 1795 vs br;  $\nu(\text{CO})$  (THF) 1926 s, 1905 vs, 1826 vs b; other bands, 2960 m sh, 2932 m sh, 2872 m, 1480 m, 1465 mw, 1451 mw, 1420 w, 1380 m, 1150 w, 1105 w, 1022 w, 880 m, 813 s, 740 m, 660 s, 642 m, 618 s, 552 w, 535 w, 496 m, 460 w;  $\nu_{\text{as}}(\text{AuCr})$  194 s. Anal. Calcd for  $\text{C}_{32}\text{H}_{46}\text{AuCr}_2\text{NO}_6$  ( $M_r = 841.68$ ): C, 45.67; H, 5.51; N, 1.66. Found: C, 45.6; H, 5.45; N, 1.75.

**Tetraethylammonium Bis(tricarbonyl( $\eta$ -cyclopentadienyl)molybdeno)aurate(I) (4)**. A procedure similar to that for **1** was followed, using  $\text{Na}[\text{Mo}(\text{CO})_3\text{Cp}]$  (5 mmol), prepared from  $[\text{Mo}(\text{CO})_3\text{Cp}]_2$  (1.22 g, 2.5 mmol). Pale yellow microcrystals of the product were obtained: yield 1.67 g, 2.04 mmol (82% based on Au); mp  $136^\circ\text{C}$ . IR<sup>71</sup> ( $\text{cm}^{-1}$ ):  $\nu(\text{CO})$  1901 vs, 1817 vs br;  $\nu(\text{CO})$  (THF) 1937 s, 1912 vs, 1833 vs; other bands, 3114 w, 3096 w, 3010 sh, 2991 w, 1482 s, 1456 w, 1437 m, 1421 w, 1392 m, 1365 w, 1172 ms, 1105 w, 1091 w, 1068 w, 1060 w, 1006 s, 999 s, 902 mw, 835 w, 799 s, 784 m, 609 m, 594 m, 572 vs, 504 s, 485 s, 442 m, 430 w, 362 w, 342 m, 327 sh;  $\nu(\text{AuMo})$  170 s; 102 w. Anal. Calcd for  $\text{C}_{24}\text{H}_{30}\text{AuMo}_2\text{NO}_6$  ( $M_r = 817.35$ ): C, 35.27; H, 3.70; N, 1.71. Found: C, 34.7; H, 3.6; N, 1.7.

**Tetra-*n*-butylammonium Bis(tricarbonyl( $\eta$ -cyclopentadienyl)tungstenio)aurate(I) (5)**. A procedure similar to that for **3** was followed, using  $\text{Na}[\text{W}(\text{CO})_3\text{Cp}]$  (2 mmol), prepared from  $[\text{W}(\text{CO})_3\text{Cp}]_2$  (0.666 g, 1 mmol). Pale yellow microcrystals of **4** were obtained: yield 0.70 g, 0.63 mmol (63% based on Au); mp  $142^\circ\text{C}$ . IR<sup>71</sup> ( $\text{cm}^{-1}$ ):  $\nu(\text{CO})$  1928 s, 1896 vs, 1810 vs br;  $\nu(\text{CO})$  (THF) 1933 s, 1905 vs, 1821 vs br; other bands, 2968 m, 2936 mw, 2876 m, 1482 m, 1466 mw, 1452 mw, 1415 m, 1380 m, 1150 w, 1103 m, 1058 w, 1024 w, 1005 w, 880 m, 810 s, 742 m, 660 s, 590 m, 565 s, 487 s, 461 m;  $\nu_{\text{as}}(\text{AuW})$  152 s. Anal. Calcd for  $\text{C}_{32}\text{H}_{46}\text{AuNO}_6\text{W}_2$  ( $M_r = 1105.39$ ): C, 34.77;

H, 4.19; N, 1.27. Found: C, 34.6; H, 4.14; N, 1.33.

**Tetra-*n*-butylammonium Bis(dicarbonyl( $\eta$ -cyclopentadienyl)ferrio)aurate(I) (6)**. To a stirred suspension of  $[\text{n-Bu}_4\text{N}][\text{AuBr}_2]$  (1.50 g, 2.5 mmol) in THF (10 mL), placed in a dry ice/acetone bath, was added a filtered solution of  $\text{Na}[\text{Fe}(\text{CO})_2\text{Cp}]$  (5 mmol) in THF (50 mL) prepared from  $[\text{Fe}(\text{CO})_2\text{Cp}]_2$  (0.89 g, 2.5 mmol). After 0.5 h of stirring, the reaction mixture was brought to room temperature and further stirred for 0.3 h. Addition of  $\text{Et}_2\text{O}$  (60 mL) precipitated an orange powder that was filtered, washed, and dried as described above (see 1). This afforded pure **5**: yield 1.61 g, 2.03 mmol (81% based on Au); mp  $60\text{--}65^\circ\text{C}$ . IR<sup>71</sup> ( $\text{cm}^{-1}$ ):  $\nu(\text{CO})$  1912 vs, 1899 vs, 1840 vs;<sup>72</sup>  $\nu(\text{CO})$  (Nujol) 1911 vs, 1897 vs, 1839 vs;  $\nu(\text{CO})$  (THF) 1923 vs, 1905 m sh, 1871 s;<sup>72</sup> other bands, 2966 ms, 2938 m, 2878 m, 1482 s, 1438 m, 1380 m, 1314 w, 1151 w, 1107 m, 1063 w, 1015 w, 1000 w, 882 m, 840 sh, 820 s, 742 m, 655 s, 604 w, 598 w, 575 vs, 561 sh, 527 w, 505 w, 375 m, 346 w;  $\nu_{\text{as}}(\text{AuFe})$  193 vs; 112 w, 99 w. Anal. Calcd for  $\text{C}_{30}\text{H}_{46}\text{AuFe}_2\text{NO}_4$  ( $M_r = 793.36$ ): C, 45.42; H, 5.84; N, 1.76. Found: C, 45.6; H, 5.75; N, 1.83.

**B. X-ray Crystallographic Study of  $[\text{n-Bu}_4\text{N}][\text{Au}(\text{Cr}(\text{CO})_3\text{Cp})_2]$  (3)**. Single crystals of **3** were obtained from  $\text{CH}_2\text{Cl}_2$ /pentane at  $-20^\circ\text{C}$ .<sup>73,74</sup> The final positional and thermal parameters are given in Table II. A table listing the observed and calculated structure factor amplitudes of the reflections used in the refinement is available as supplementary material.<sup>75</sup>

**C. Mössbauer Data**. The trimetallic  $[\text{M}'\text{-Au-M}']^-$  complexes were prepared as described in this work and the  $[\text{X-Au-X}]^-$  anions as reported in the literature.<sup>24</sup> Samples were handled under nitrogen in a dry glovebox. The Mössbauer spectra have been measured on conventional sinus drives keeping both source and absorbers at 4.2 K. The <sup>197</sup>Pt activity was obtained by irradiating 300 mg of natural platinum for 8 h in a neutron flux of  $10^{12}$  n/( $\text{cm}^2$  s). The 77.3-keV  $\gamma$ -ray was detected either with a 5-mm NaI or a Ge-Li detector. The carefully ground samples (typical absorber thickness 100 mg/ $\text{cm}^2$ ) were encapsulated in tight aluminum holders. The experimental data have been least-squares fitted as a sum of two lines of Lorentzian shape with independent intensities and widths.

The source has been tested against a natural gold foil in order to check that the measured parameters are identical with those reported in the literature. The spectra of the auroic complexes studied in the present work consist of two lines with equal widths at half-maximum but different intensities. Noteworthy, the line of lower energy has always a larger intensity although care has been taken in grinding the absorber material with carbon boride powder. A similar asymmetry of the resonance spectra has been reported earlier in other linear Au(I) complexes<sup>61,76</sup> and originates most probably from the anisotropy of the lattice vibration of the gold atom within the molecular frame.

Table IV summarizes the results of the fit of the experimental data, and a typical spectrum is shown in Figure 2 for **1**.

**Acknowledgment**. P.B. is very grateful to Drs. J. M. Friedt and J. P. Sanchez of the Laboratoire de Chimie Nucléaire, Centre de Recherches Nucléaires du CNRS associé à l'

(72) Two absorptions at 2001 and 1768  $\text{cm}^{-1}$  (KBr) or at 1990 and 1780  $\text{cm}^{-1}$  (THF) progressively appear and grow in intensity as a function of time due to product decomposition into *cis*- $[\text{FeCp}(\text{CO})_2]$ .<sup>26</sup> This can be prevented by preparing Nujol mulls under nitrogen.

(73) Cell dimensions were obtained on a Syntex P2<sub>1</sub> four-circle diffractometer by centering and subsequent refinement of 15 high-angle reflections from different parts of the reciprocal space at room temperature:  $a = 1110.6$  (6) pm,  $b = 1690.5$  (14) pm,  $c = 2209.2$  (8) pm,  $\beta = 122.46$  (3) $^\circ$ , space group  $P2_1/c$ ,  $Z = 4$ , calculated density 1.60 g/ $\text{cm}^3$ . Intensity data were collected from a needle-shaped crystal of the size  $0.1 \times 0.1 \times 0.4$  mm between  $2^\circ \leq 2\theta \leq 45^\circ$  (4154 independent reflections,  $\omega$  scan, Mo K $\alpha$  radiation,  $\lambda = 71.069$  pm, graphite monochromator). Lorentz, polarization, and an empirical absorption correction were applied.

(74) The positions of the metal atoms were located from a Patterson function. Subsequent difference Fourier maps revealed the positions of the carbon, oxygen, and nitrogen atoms. The positions of most of the hydrogen atoms were calculated according to ideal geometry. Due to the paucity of observed reflections (1524 structure factors with  $F_o \geq 3.8\sigma(F_o)$ ), caused by the small crystal size, only the metal atoms could be refined with anisotropic thermal parameters (full-matrix least squares; scattering factors for the neutral atoms according to "International Tables of Crystallography"; hydrogen parameters not refined). The rather poor  $R_1 = R_2 = 0.103$  has to be attributed to the fact that the light atoms having high thermal motion could not be refined anisotropically.

(75) See paragraph at the end of paper regarding supplementary material.  
(76) Pfeiffer, L.; Raghavan, R. S.; Lichtenwainer, C. P.; West, K. W. *Phys. Rev. Lett.* 1973, 30, 635.

(71) Intensities of the absorption bands are designated (in parentheses) as follows: vs, very strong; s, strong; w, weak; vw, very weak; sh, shoulder.



Université Louis Pasteur, Strasbourg, for the  $^{197}\text{Au}$  Mössbauer data collection and for their valuable comments. The CNRS is acknowledged for financial support and Johnson-Matthey and Co. Limited for a generous loan of  $\text{Na}[\text{AuCl}_4] \cdot x\text{H}_2\text{O}$ .

**Registry No.** 1, 56048-16-9; 2, 56048-15-8; 3, 76796-11-7; 4, 56048-23-8; 5, 77188-24-0; 6, 92543-72-1;  $[\text{Et}_4\text{N}][\text{AuCl}_2]$ , 50480-98-3;  $\text{NaMn}(\text{CO})_5$ , 13859-41-1;  $[\text{Et}_4\text{N}][\text{AuBr}_2]$ , 50481-00-0;  $\text{NaCo}(\text{CO})_4$ , 14878-28-5;  $[n\text{-Bu}_4\text{N}][\text{AuBr}_2]$ , 50481-01-1;  $\text{Na}[\text{Cr}(\text{CO})_3\text{Cp}]$ ,

12203-12-2;  $\text{Na}[\text{Mo}(\text{CO})_3\text{Cp}]$ , 12107-35-6;  $\text{Na}[\text{W}(\text{CO})_3\text{Cp}]$ , 12107-36-7;  $\text{Na}[\text{Fe}(\text{CO})_2\text{Cp}]$ , 12152-20-4;  $[n\text{-Bu}_4\text{N}][\text{AuCl}_2]$ , 50480-99-4;  $[n\text{-Bu}_4\text{N}][\text{AuI}_2]$ , 50481-03-3; Mn, 7439-96-5; Co, 7440-48-4; Cr, 7440-47-3; Mo, 7439-98-7; W, 7440-33-7; Fe, 7439-89-6; Au, 7440-57-5.

**Supplementary Material Available:** Calculated hydrogen coordinates (Table V), anisotropic thermal parameters (Table VI), and observed and calculated structure factors for 3 (Table VII) (21 pages). Ordering information is given on any current masthead page.

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## Platinum(II) Complexes of Unsymmetrical, Potentially Bidentate Ligands

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The reactions of a series of unsymmetrical, potentially bidentate ligands  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{X}$  ( $n = 2$ ,  $\text{X} = \text{OMe}$ ,  $\text{NMe}_2$ ,  $\text{SMe}$ ;  $n = 3$ ,  $\text{X} = \text{NMe}_2$ ) with  $[\text{PtX}_2(\text{cod})]$  ( $\text{X} = \text{Cl}$ ,  $\text{I}$ ) are described. The tendency of the ligand to bond to the metal in a bidentate fashion is dependent on the nature of the weak donor, and on the size of the chelate ring formed. Halide abstraction by  $\text{Ag}^+$  promotes coordination of the ether function to yield  $[\text{PtCl}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{OMe})_2]^+$  and  $[\text{Pt}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{OMe})_2]^{2+}$ . Reactions of the former with a number of weak donor ligands have been studied by  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy. Complex mixtures are obtained with  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{SMe}$ , and the involvement of ion-paired species is suggested in this case.

### Introduction

The use of transition-metal complexes to catalyze transformations involving unsaturated organic substrates such as olefins or acetylenes is widespread, yet the stability constants for the formation of metal-olefin and -acetylene complexes are generally low.<sup>1</sup> Thus, in order to obtain greater catalytic activities, complexes containing weak donor ligands that may be readily displaced by the unsaturated species have been employed.<sup>2</sup> The idea of preparing low-valent transition-metal complexes containing mixed bidentate ligands, which exhibit one strong and one weak donor function, is one that has been advanced in the last few years.<sup>3</sup> The utility of such ligands in terms of homogeneous catalysis lies in the susceptibility of the weak donor to displacement by a substrate molecule, whereas the chelate effect confers additional stability on the catalyst precursor in the absence of the substrate.

In this paper we report the preparation of a series of such ligands,  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{X}$  ( $n = 2$ ,  $\text{X} = \text{OMe}$ ,  $\text{NMe}_2$ ,  $\text{SMe}$ ;  $n = 3$ ,  $\text{X} = \text{NMe}_2$ ), and the formation and reactions of their platinum(II) complexes.  $^{13}\text{C}\{^1\text{H}\}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopies have been employed to characterize the ligands, and the solution chemistry of the platinum(II) complexes has been studied with  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy.

### Experimental Section

The  $^{13}\text{C}\{^1\text{H}\}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra were recorded at 25.1 and 40.2 MHz, respectively, on a JEOL FX-100 spectrometer operating in the Fourier transform mode and were obtained for  $\text{CDCl}_3$  solutions unless otherwise stated. Infrared spectra were measured from KBr pellets using a Perkin-Elmer 521 spectrophotometer. Microanalyses

were performed by Galbraith Microanalytical Laboratories, Knoxville, TN.

The compounds  $\text{ClCH}_2\text{CH}_2\text{OMe}$ ,  $\text{Cl}(\text{CH}_2)_n\text{NMe}_2 \cdot \text{HCl}$  ( $n = 2, 3$ ), and  $\text{ClCH}_2\text{CH}_2\text{SMe}$  were obtained from Aldrich. The free amines were generated by treating the hydrochlorides with KOH, extracting with ether, and drying over  $\text{Na}_2\text{SO}_4$ . The ether and thioether were used without further purification. Tetrahydrofuran was distilled from sodium benzophenone ketyl immediately prior to use.

**2-(Diphenylphosphino)ethyl Methyl Ether,  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{OMe}$ .**<sup>4</sup> 2-Chloroethyl methyl ether (10.3 g, 0.11 mol) was added dropwise to a solution of  $\text{LiPPh}_2$  (24 g, 0.12 mol) (prepared from lithium and chlorodiphenylphosphine) in dry THF (250 mL) under nitrogen at 0 °C. The mixture was allowed to warm to ambient temperature and stirred for 30 min. Deoxygenated water (100 mL) was added slowly, the organic layer was separated, and the solvent was evaporated. The residual viscous oil was distilled under reduced pressure (bp 164 °C (0.5 torr)) to give  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{OMe}$  as a colorless oil; yield 15.0 g (56%).

The following were prepared analogously:  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{NMe}_2$  (bp 160 °C (0.5 torr)), obtained as a colorless oil in 51% yield;  $\text{Ph}_2\text{P}(\text{CH}_2)_3\text{NMe}_2$  (bp 174–180 °C (0.5 torr)), obtained as a colorless oil in 72% yield;  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{SMe}$  (bp 148–154 °C (0.5 torr)), obtained as a colorless oil that solidified on standing, in 66% yield.

***cis*- $[\text{PtCl}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{OMe})_2]$ .** To a solution containing  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{OMe}$  (1.30 g, 5.33 mmol) in chloroform (50 mL) was added  $[\text{PtCl}_2(\text{cod})]$  (1.00 g, 2.67 mmol). The mixture was stirred for 15 min, and diethyl ether was added slowly to initiate crystallization. The product was filtered and washed with ether (50 mL) to give *cis*- $[\text{PtCl}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{OMe})_2]$  as colorless crystals: yield, 1.60 g (79%); mp 192 °C. Anal. Calcd for  $\text{C}_{30}\text{H}_{34}\text{Cl}_2\text{O}_2\text{P}_2$ : C, 47.77; H, 4.53. Found: C, 47.70; H, 4.63.

***cis*- $[\text{PtCl}_2(\text{Ph}_2\text{P}(\text{CH}_2)_3\text{NMe}_2)_2]$ .** This complex was compared as above and isolated as pale yellow crystals: yield, 74%; mp >200 °C. Anal. Calcd for  $\text{C}_{34}\text{H}_{44}\text{Cl}_2\text{N}_2\text{P}_2$ : C, 50.76; H, 5.48. Found: C, 50.53; H, 5.41.

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