

diffraction patterns were identical. Curves B-D in Figure 2 for three tetragonal samples show some partial metallic behavior over a limited range of temperature, along with semiconducting behavior at lower temperatures, and very broad superconducting transitions beginning below 70 K and finishing below 50 K. One sample (curve D), however, retained semiconducting behavior without a superconducting transition down to 15 K, which is the lowest temperature attained in these measurements. The room temperature resistivities of these three samples were estimated to be ~ 500 (B), 13 000 (C), and 30 000 $\mu\Omega$ cm (D). While we cannot rule out the presence of a small amount of the orthorhombic phase (<5%) as being responsible for these anomalous conductive properties, we believe that these properties are due to different oxygen content in the tetragonal-phase samples. However, we do not find the tetragonal phase to be the 93 K superconductor.

In summary, we have demonstrated that, in the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ superconductor sample, the cooling rate subsequent to oxygen annealing is a very critical factor in obtaining the high- T_c superconducting orthorhombic phase.

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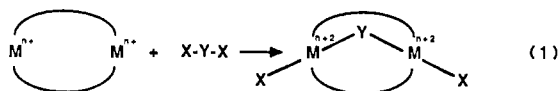
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Three-Fragment, Two-Centered Oxidative Addition of AuCl_4^- to $\text{Ir}_2(\text{CO})_2\text{Cl}_2(\mu\text{-}(\text{Ph}_2\text{PCH}_2)_2\text{AsPh})_2$

Sir:

The two-center, three-fragment oxidative-addition reaction (eq 1) is relatively rare. The binuclear complex $\text{Pd}_2(\text{dpm})_3$ (dpm is



bis(diphenylphosphino)methane) undergoes such reactions under both thermal¹ and photochemical² activation with a variety of organic dihalides including dihalomethanes, 1,2-diodobenzene, dichlorophenyl isocyanide, and oxalyl chloride. Examples of the addition of dihalomethanes to a number of other metal complexes are also known.³ Since the oxidative additions of metal-halogen bonds to a single metal center are known,⁴ dihalometal complexes should also be able to participate (as X-Y-X) in reaction 1. Here we report the first example of such a reaction, one in which AuCl_4^- acts as X-Y-X and two new metal-metal bonds are formed.

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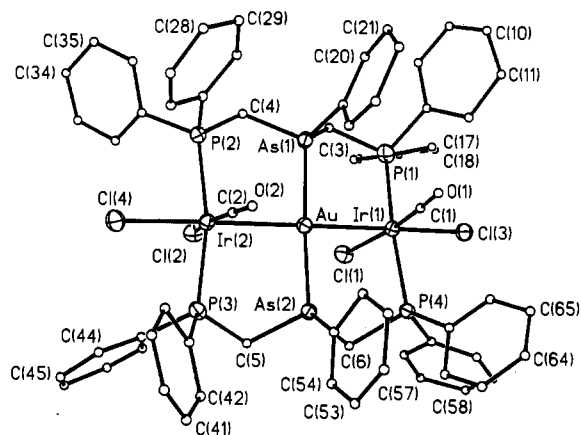
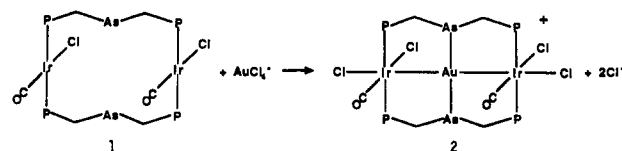


Figure 1. Perspective view of $[\text{Ir}_2\text{Au}(\text{CO})_2\text{Cl}_4(\mu\text{-dpma})_2]^+$ showing 50% thermal ellipsoids for heavy atoms and arbitrarily sized, uniform circles for all carbon and oxygen atoms. Selected distances (\AA) and angles (deg): Au-Ir(1), 2.812 (2); Au-Ir(2), 2.806 (2); Au-As(1), 2.379 (4); Au-As(2), 2.386 (4); Ir(1)-P(1), 2.390 (9); Ir(1)-P(4), 2.364 (9); Ir(1)-C(1), 1.88 (3); Ir(1)-Cl(1), 2.400 (7); Ir(1)-Cl(3), 2.455 (7); Ir(2)-P(2), 2.366 (10); Ir(2)-P(3), 2.366 (9); Ir(2)-C(2), 1.77 (3); Ir(2)-Cl(2), 2.395 (7); Ir(2)-Cl(4), 2.477 (8), Ir(1)-Au-Ir(2), 173.1 (1); As(1)-Au-As(2), 175.0 (1); As(1)-Au-Ir(1), 87.4 (1); As(1)-Au-Ir(2), 91.7 (1); As(2)-Au-Ir(1), 91.8 (1); As(2)-Au-Ir(2), 89.7 (1); P(1)-Ir(1)-P(4), 164.9 (3); Cl(1)-Ir(1)-C(1), 167 (1); Au-Ir(1)-Cl(3), 179.7 (2); P(2)-Ir(2)-P(3), 167.5 (3); Cl(2)-Ir(2)-C(2), 166.7 (9); Au-Ir(2)-Cl(4), 176.2 (2).

Addition of a yellow dichloromethane solution of $[\text{Ph}_4\text{As}][\text{AuCl}_4]$ to a yellow solution of $\text{Ir}_2(\text{CO})_2\text{Cl}_2(\mu\text{-dpma})_2$ (**1**)⁵ (dpma



(2)

is bis((diphenylphosphino)methyl)phenylarsine) produces a bright red solution from which red needles of $[\text{Ir}_2\text{Au}(\text{CO})_2\text{Cl}_4(\mu\text{-dpma})_2]\text{Cl}$ (**2**) precipitate in 84% yield upon the addition of ethyl ether. The ³¹P NMR spectrum shows a singlet at -8.4 ppm (vs. 18.4 ppm for **1**). The infrared spectrum shows a terminal carbonyl absorption at 2011 cm^{-1} . The increase in $\nu(\text{CO})$ over that in **1** (1964 cm^{-1}) is indicative of oxidation of iridium although the increase is rather small.⁶

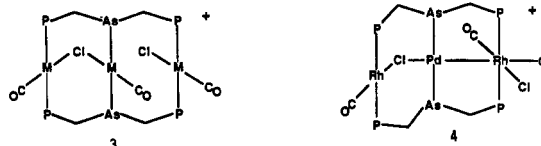
The structure of **2** has been determined by an X-ray diffraction study.⁷ A perspective view of the cation is shown in Figure 1. The chloride counterion, Cl(5), is not coordinated to the cation; the shortest Au...Cl(5) separation is 6.41 \AA . The cation has effective (noncrystallographic) C_{2v} symmetry with the 2-fold axis passing through the gold atom, perpendicular to the $\text{Ir}_2\text{Au}(\text{C}-\text{O})_2\text{Cl}_4$ plane. The two iridium ions are six-coordinate while the gold ion is four-coordinate and planar. The positioning of Cl(3) and Cl(4) clearly shows that oxidative addition has occurred while the two arsenic atoms have replaced two of the chloride ions in the coordination of the gold ion. The Au-As distances (2.379 (4), 2.386 (4) \AA) are similar to the Au-As distance in Ph_3AsAuBr (2.342 (5) \AA).⁸ The Au-Ir distances (2.812 (2), 2.806 (2) \AA) are nearly equivalent and are just slightly longer than the range of other Au-Ir single bonds.⁹ The coordination of the two iridium

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- Red crystals of $[\text{Ir}_2\text{Au}(\text{CO})_2\text{Cl}_4(\mu\text{-dpma})_2]\text{Cl}$ were grown by diffusion of ethyl ether into a dichloromethane solution of **2**. They belong to the monoclinic space group $P2_1/c$ (No. 14) with $a = 13.346$ (2) \AA , $b = 12.794$ (5) \AA , $c = 44.82$ (3) \AA , $\beta = 98.29$ (4) $^\circ$ at 130 K with $Z = 4$. Refinement of 3106 reflections with $I > 3\sigma(I)$ with 399 parameters yielded $R = 0.0666$ and $R_w = 0.0747$.
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ions is quite normal. The elongation of the Ir-Cl bonds that are trans to the Au-Ir bonds relative to the cis Ir-Cl bonds is consistent with the high structural trans influence of metal-metal bonds and previous observations.¹⁰

An Au(III) ion coordinated between two Ir(I) centers may be regarded (after oxidative addition) as an Ir(II)-Au(I)-Ir(II) system, in which the electron count around each Ir(II) is 18 and that around the Au(I) is 16. Planar coordination, however, is highly unusual for Au(I), but four-coordinate gold complexes with 16 electrons are planar whereas those with 18 electrons are tetrahedral,¹¹ so **2** follows the general pattern.

The behavior of $\text{Ir}_2(\text{CO})_2\text{Cl}_2(\mu\text{-dpma})_2$ and its rhodium analogue, $\text{Rh}_2(\text{CO})_2\text{Cl}_2(\mu\text{-dpma})_2$, toward other d^8 metal complexes shows different reactivity. Addition of Rh(I) or Ir(I) complexes produces **3** in which a stack of three d^8 ions forms and no oxidative



addition occurs.¹² Reaction with Pd(II) (from $(\text{PhCN})_2\text{PdCl}_2$) produces **4** in which one Pd-Cl bond has been added to one, but only one, of the two metal centers; the metal ion at the other end of the molecule is left unaffected.^{5,13} Since with Au(III) the three-fragment, two-center oxidative addition occurs, there appears to be a simple trend in which increasing the oxidation state of the added metal increases the number of oxidative-addition reactions.

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Supplementary Material Available: Tables summarizing the data collection and refinement, atom coordinates, bond distances, bond angles, anisotropic thermal parameters, and hydrogen coordinates (10 pages). Ordering information is given on any masthead page.

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- (11) (a) Puddephatt, R. J. *The Chemistry of Gold*; Elsevier: Amsterdam, 1978. (b) The salt $\text{TiAu}(\text{CN})_2$ is somewhat of an exception since short Au-Au contacts, 3.037 (4) and 3.068 (4) Å, about each $\text{Au}(\text{CN})_2^-$ produce a planar coordination environment (Blom, N.; Ludi, A.; Burgi, H.-B.; Tichy, K. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1984**, *C40*, 1767). $[\text{AuOs}_6(\text{CO})_{20}\text{H}_2]^{2-}$ contains a planar AuOs_4 unit (Johnson, B. F. G.; Kaner, D. A.; Lewis, J.; Ruithby, P. R. *J. Chem. Soc., Chem. Commun.* **1981**, 753), and $\text{Au}_2[\text{Ph}_2\text{PCH}(\text{CH}_2\text{OCH}_3)\text{-PPh}_2]_2\text{Cl}^+$ contains one planar $\text{Au}(\text{P}_2\text{ClAu})$ unit with long Au-Au (3.002 (1) Å) and Au-Cl (2.963 (3) Å) distances (Schmidbauer, H.; Pollok, T.; Herr, R.; Wagner, F. E.; Bau, R.; Riede, J.; Muller, G. *Organometallics*, **1986**, *5*, 569).

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Articles

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Formation and Reactivity of Palladium(II) Sulfite Complexes in Aqueous Solution. 1. Spectroscopic Evidence for the Labilization of a Chelated Amine

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The reactions of $\text{Pd}(\text{Et}_4\text{dien})\text{Cl}^+$ and $\text{Pd}(\text{Et}_4\text{dien})\text{OH}_2^{2+}$ (Et_4dien = 1,1,7,7-tetraethyldiethylenetriamine) with bisulfite/sulfite were studied as a function of pH and sulfite concentration with use of spectroscopic techniques, viz. UV-vis, IR, and ^1H and ^{13}C NMR spectroscopy. The results clearly demonstrate the formation of $\text{Pd}(\text{Et}_4\text{dien})\text{SO}_3$, which is stable at $\text{pH} > 7$ but dechelates in acidic medium ($\text{pH} < 6$) to produce a mixture of $\text{Pd}(\text{SO}_3)_2^{2-}$ and $\text{Pd}(\text{SO}_3)_3^{4-}$ depending on the sulfite concentration employed. The dechelation reaction is reversible; i.e., addition of base to $\text{pH} > 8$ regenerates the $\text{Pd}(\text{Et}_4\text{dien})\text{SO}_3$ species completely. The results are interpreted in terms of the labilization effect of coordinated sulfite and stabilization of the released amine ligand via protonation to prevent the reverse chelation reaction.

Introduction

We have a longstanding interest in the chemistry and mechanistic behavior of transition-metal carbonate and sulfite complexes in aqueous solution.¹⁻⁶ Our earlier work focused on octahedral complexes of Co(III), Rh(III), and Cr(III), and we recently extended these studies to square-planar complexes of Pt(II) and Pd(II). Surprising was our finding³ that, in contrast to the case for octahedral complexes, the carbonate complexes of diethylenetriamine (dien) and substituted dien species of Pd(II) are not formed via the well-known CO_2 uptake by the metal hydroxo

species but rather via anation of the metal aquo species by HCO_3^- or CO_3^{2-} . In a subsequent study⁷ we could find no evidence for the formation of the corresponding Pt(II) carbonate complexes. These observations were partly ascribed to the nature of the

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