The worst situation is when the positive and negative sites alternate as in DAP and imides. G–C represents the intermediate case, while in the most favorable situation one molecule has all of the hydrogen-bond donor sites and the other has all of the acceptor sites. The general validity of this simple concept is unequivocally supported by the following dipeptide model (Chart III). The optimizations for the planar structures used the same charges in both forms.[7] The hydrogen bonding in the retro-inverso isomer is favored by 11 kcal/mol, owing again to the net difference of four secondary interactions. Such considerations have general applicability in understanding variations in hydrogen-bonding complexation in many contexts.[16]

Supplementary Material Available: Listing of parameters for nucleic acid bases and DAP in the all-atom OPLS force field, graphical summary of the charge distributions for the parent nucleic acid bases, and a plot showing the progress of the three mutations used to compute the relative free energy of binding for G–C vs U–DAP in chloroform (5 pages). Ordering information is given on any current masthead page.

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(16) Gratitude is expressed to the National Institutes of Health (GM32136) for support of this research.

Chelate Ring Opening and Metal Ion Relocation Leading to the Formation of a Luminescent $Au^IIr^IAu^I$ Chain Complex

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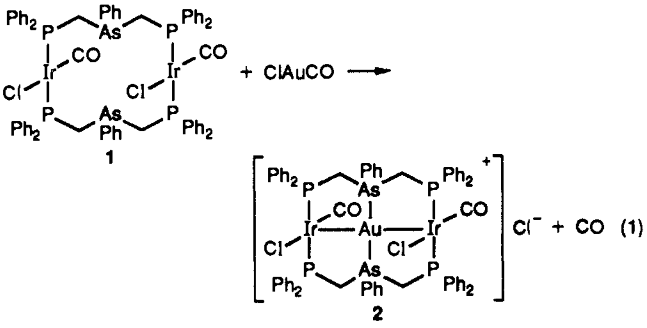
Recently we have developed rational routes to the synthesis of heterotrinuclear complexes using binuclear metallomacrocycles as precursors.[1] Equation 1 shows an example involving the incorporation of gold into a diiridium macrocycle **1**.[2] The metallomacrocycle **1** has considerable stability; for example, it is capable of extracting some metal ions from aqueous solution into dichloromethane.[3] Here we describe a new and unexpected route to the formation of a related heterotrinuclear complex. This method also uses bis[(diphenylphosphino)methyl]phenylarsine (dpma) as a bridge, but involves much more bond reorganization than encountered in eq 1.

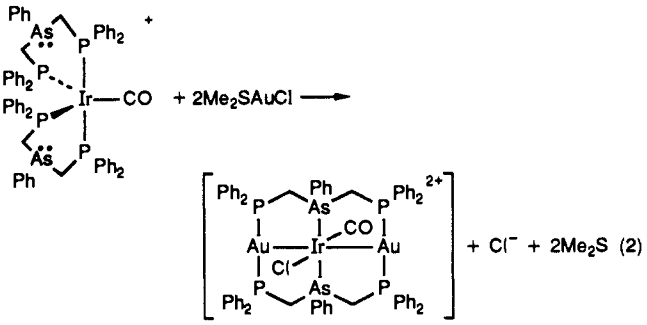


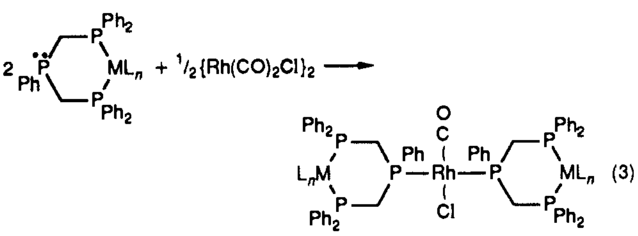
1

2

Treatment of $Ir(CO)_2Cl$ (*p*-toluidine) in methanol with 2 equiv of dpma in dichloromethane followed by an excess of ammonium hexafluorophosphate in methanol produces, after partial evaporation of the solvent, ivory crystals of $[Ir(CO)(dpma)_2][PF_6]$ (**3**) in 76% yield. The structure of the trigonal-bipyramidal cation is shown in Figure 1. It is similar to other cations with an $Ir(CO)P_4$ core.[5]

Addition of 2 equiv of Me_2SAuCl in dichloromethane to a dichloromethane solution of **3** produces a red solution, from which red crystals of $[Au_2Ir(CO)Cl(\mu\text{-dpma})_2][PF_6]_2$ (**4**)[6] can be isolated in 84% yield by the addition of a methanol solution of ammonium hexafluorophosphate followed by partial evaporation of the solvent (eq 2). The structure of the cation of **4**, as determined by X-ray crystallography, is shown in Figure 1. Notice that the metal ion locations in **4** and **2** have an inside-out relationship. While **3** incorporates the correct Ir:dpma:CO stoichiometry for the formation of **4**, reaction 2 leaves only one metal ligand bond, the Ir–CO bond, intact.[1] All four of the Ir–P bonds in **3** and the Au–S and Au–Cl bonds are broken in this high-yield reaction. This represents quite a remarkable set of changes that contrasts with the much more conservative group of changes in eq 1. While chelate ring opening of four-membered rings, especially those involving bis(diphenylphosphino)methane, to form binuclear complexes is known,[7] opening of the less strained six-membered rings in **3** is wholly unexpected. Prior work showed that reactions of analogous triphosphine complexes resulted in formation of bi- or trinuclear complexes with widely separated metal centers by bonding to the uncoordinated donor without ring opening (eq 3).[8] We have monitored reaction 2 by ^{31}P NMR spectroscopy at −60 °C, but only the slow conversion of the starting material to the product is observed. No intermediates in this complex transformation are observable.





$ML_n = Pt(CH_3)_2, PtCl_2, PdCl_2, Mo(CO)_4$

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(4) IR: $\nu(CO)$, 1925 cm^{-1}. $^{31}P\{^1H\}$ NMR: δ −21.8 (t), −29.1 (t) [$J(P,P)$ = 28.8 Hz]. Ivory crystals of $[Ir(CO)(dpma)_2]PF_6\cdot CH_2Cl_2\cdot(C_2H_5)_2O$ were grown by diffusion of ethyl ether into a dichloromethane solution of **3**. They belong to the orthorhombic space group *Pbnb* (No. 56) with a = 16.487 (4) Å, b = 26.297 (7) Å, and c = 30.733 (6) Å at 130 K, Z = 8, R = 0.067, and R_w = 0.065 for 5274 reflections with $I > 2\sigma(I)$ and 410 parameters.

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(6) IR: $\nu(CO)$, 1971 cm^{-1}. $^{31}P\{^1H\}$ NMR: δ = 34.2 (s). Red crystals of $[Au_2Ir(CO)Cl(\mu\text{-dpma})_2][PF_6]_2\cdot CH_2Cl_2$ were obtained with difficulty by diffusion of ethyl ether into a dichloromethane solution of the complex. They belong to the triclinic space group $P\bar{1}$ with a = 12.218 (4) Å, b = 24.768 (8) Å, c = 26.693 (9) Å, α = 112.75 (2)°, β = 91.65 (3)°, and γ = 95.50 (3)° at 130 K, Z = 4, R = 0.101, and R_w = 0.101 for 11 583 reflections with $F > 4\sigma(F)$ and 852 parameters. There are two independent cations, four independent anions, and 2.5 molecules of CH_2Cl_2 in the asymmetric unit.

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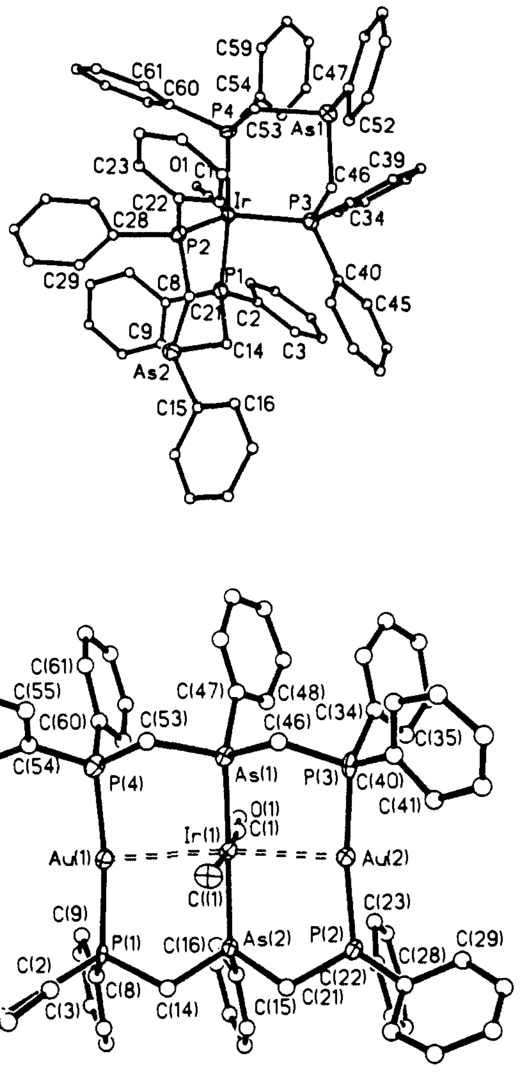

Figure 1. Top: Cation of **3**, $[Ir(CO)(dpma)_2]^+$; bond distances (angstroms), Ir–P(1), 2.367 (4); Ir–P(2), 2.400 (4); Ir–P(3), 2.358 (4); Ir–C(1), 1.853 (4); Ir···As(1), 4.316 (2); Ir···As(2), 4.384 (2); angles (degrees), P(1)–Ir–P(4), 169.1 (1); P(2)–Ir–P(3), 108.1 (1); P(2)–Ir–C(1), 127.3 (4); P(3)–Ir–C(1), 124.6 (4). Bottom: cation of **4**, $[Au_2Ir(CO)Cl(\mu\text{-dpma})_2]^+$; bond distances (angstroms), Au(1)–Ir(1), 3.013 (2), 3.014 (2); Au(2)–Ir(1), 2.985 (2), 3.025 (2); Au(1)–P(1), 2.318 (10), 2.306 (9); Au(1)–P(4), 2.306 (10), 2.303 (10); Au(2)–P(2), 2.286 (10), 2.318 (10); Au(2)–P(3), 2.315 (10), 2.297 (9); Ir(1)–As(1), 2.409 (4), 2.416 (4); Ir(1)–As(2), 2.407 (4), 2.408 (4); Ir(1)–Cl(1), 2.384 (11), 2.381 (10); Ir(1)–C(1), 1.78 (4), 1.84 (4); angles (degrees), Au(1)–Ir(1)–Au(2), 157.7 (1), 152.6 (1); P(1)–Au(1)–P(4), 169.4 (4), 173.8 (4); P(2)–Au(2)–P(3), 167.7 (4), 161.7 (4); As(1)–Ir(1)–As(2), 170.0 (2), 170.6 (2).

Significant Au–Ir interactions exist within **4**. The Au–Ir distances are nearly equal, and the Au–Ir–Au angle is slightly bent. The electronic absorption spectrum of **4** shown in Figure 2 shows that the $IrP_2Cl(CO)$ chromophore [which has λ_{max} = 438, 387, 339 in $Ir(CO)Cl(PPh_3)_2]^9$ is strongly perturbed by the proximity of the two gold ions. The spectrum is remarkably similar to that of **2** (λ_{max} = 508, ϵ = 32 000). Complex **4** is strongly luminescent in solution. As seen in Figure 2, there are two emission bands, both of which have excitation profiles that resemble the absorption spectrum. The high-energy emission is attributed to fluorescence while the lower energy band is probably due to phosphorescence. The temperature dependence of the spectrum supports this assignment. On cooling to −196 °C, the intensity of the low-energy emission increases relative to that of the higher energy emission as shown in Figure 2. These electronic

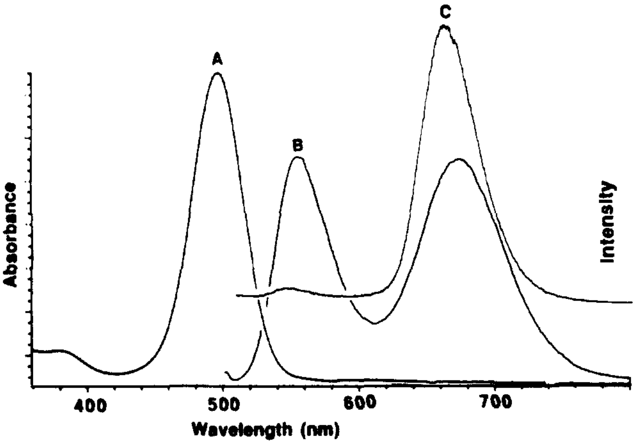

Figure 2. A, electronic absorption (λ_{max} = 498 nm, ϵ = 31 400 L mol^{-1} cm^{-1}); B, uncorrected emission [λ(excitation) = 500 nm] spectra for $[Au_2Ir(CO)Cl(\mu\text{-dpma})_2][PF_6]_2$ in dichloromethane solution at 23 °C; C, uncorrected emission at 77 K.

spectral features can readily be accounted for by modifying the simple molecular orbital picture developed for the $d^8d^{10}d^8$ Ir^I–Au^I–Ir^I chain to this $d^{10}d^8d^{10}$ chain in which the predominant interactions involve the filled d_{z^2} and empty p_z orbitals that are directed along the Au–Ir–Au axis.[2]

Preliminary results indicate that **3** reacts with a variety of other transition-metal ions including Ag^I, Pd^{II}, and Ir^I. The structures and properties of the products are under investigation.

Acknowledgment. We thank the National Science Foundation (CHE-8941209 and CHE-8519557) for support, Johnson Matthey, Inc., for a loan of precious metal salts, and Professor H. Hope for experimental assistance. The diffraction and computing equipment used in this study were purchased under NSF Grant CHE-8802721 to the University of California, Davis.

Supplementary Material Available: Tables of atomic positional parameters, bond distances, bond angles, anisotropic thermal parameters, hydrogen atom positions, and data collection parameters for **3** and **4** (23 pages). Ordering information is given on any current masthead page.

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Reactivity of a Sc–Si Bond toward CO and $CN(2,6\text{-}Me_2C_6H_3)$. Generation and Reactivity of an Apparent Silene Intermediate Resulting from Isocyanide Coupling at Scandium

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Electron-deficient alkyl and silyl complexes of d^0 metals generally combine with CO or CNR (isocyanides) to form reactive η^2-COR′ or η^2-C(NR)R′ derivatives.[1,2] In some cases, products

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