Olefin Complexes of Gold(I) by CO Displacement from AuCl(CO)

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The *cis*-cyclooctene and norbornene complexes of AuCl, AuCl(*cis*-C_8H_{14}) (1) and AuCl(C_7H_{10}) (2), respectively, have been prepared from the reaction of AuCl(CO) with the corresponding olefin at room temperature by a CO displacement reaction. Gas volumetric equilibrium data on the reaction between AuCl(CO) and norbornene show that the formation of the olefin complex is favored at atmospheric pressure of carbon monoxide. The constant of the equilibrium AuCl(CO) + norbornene $\rightleftharpoons$ AuCl(norbornene) + CO is $K = 4 \pm 1$ at 21.5 °C. No CO was found to be displaced from AuCl(CO) with cyanoolefins. The crystal structure of 1 has been solved by X-ray diffraction methods. For 2, only the crystal data and a structure with insufficient resolution were obtained. The crystal data at 190 K are as follows: 1, $a = 23.115$ (4) Å, $b = 5.419$ (3) Å, $c = 7.356$ (2) Å, $Z = 4$, orthorhombic, space group $Pca2_1$, $R = 0.037$; 2, $a = 5.697$ (2) Å, $b = 20.24$ (1) Å, $c = 6.620$ (2) Å, $Z = 4$, orthorhombic, space group $Ama2$, $R = 0.085$. The gold atom presents the expected linear geometry, considering the olefin as a monodentate ligand.

Introduction

In continuation of recent studies of carbonyl derivatives of late transition elements[1] suggesting that the observed properties of these systems do not require the intervention of an important π contribution to the bond, we reasoned that also the metal–olefin bond of some of the noble metals could perhaps require some reconsideration. A recent paper has suggested[2] that the π contribution to the bond in olefin complexes of platinum(II) may be negligible, while a Hartree–Fock–Slater calculation has indicated that the importance of the π contribution may decrease along the Cu–Ag–Au sequence[3] for monovalent cations. Our synthetic work has provided a facile method of preparing AuCl(CO), which appeared to be ideally suited for studies of interactions with olefin substrates since it is monomeric in solution,[1a] with no important steric effects being involved in view of the linear geometry.[4]

Olefin complexes of gold(I) have been prepared earlier either by the reaction of tetrachloroauric acid with the olefin or directly from the olefin and AuCl.[5] No systematic studies have appeared on the competition between olefins and carbon monoxide for the coordination sphere of gold(I) or, for that matter, for any of the noble-metal cations at the extreme right of the periodic sequence.

We report that competitive equilibria for some AuCl-(CO)–olefin systems and the crystal and molecular structure of one of these compounds.

Experimental Section

All of the operations reported in this paper, were carried out under an atmosphere of dinitrogen or carbon monoxide, as specified. Solvents were carefully dried by conventional methods prior to use. Chlorocarbonylgold(I) was prepared as previously described.[1a] The IR spectra in the 4000–400 cm^{-1} region were measured with Perkin-Elmer 283 and 597 instruments and with a Bruker IFS-114C Fourier spectrophotometer between 650 and 50 cm^{-1}.

Preparation of the AuCl(olefin) Complexes. The preparation of the norbornene complex is reported in detail, that of the cyclooctene derivative being substantially identical. The gold carbonyl chloride complex, AuCl(CO), was prepared from anhydrous gold(III) chloride (4.211 g, 13.9 mmol) and carbon monoxide at atmospheric pressure in dichloromethane (100 cm^3); after 12 h of stirring at room temperature, substantially complete conversion to the carbonyl derivative was observed, as monitored by IR spectra in the carbonyl stretching region. The resulting suspension of the carbonyl derivative was treated with a dichloromethane (10 cm^3) solution of norbornene (1.4 g, 14.89 mmol) at room temperature. After 3 h of stirring at room temperature, the IR monitoring showed the absence of any residual AuCl(CO). The colorless olefin complex was recovered by evaporation to dryness of the solvent and by addition of pentane (20 cm^3); the product was filtered and dried in vacuo (4.0 g, 88% yield). The IR spectrum of the olefin complex showed absortions at 1480 w, 1450 m, and 1440 m-s cm^{-1} as poly(trichlorofluoroethylene) mull, to be compared with the bands at 1615 w, 1570 w, 1470 w, and 1450 m cm^{-1} for the uncomplexed olefin under the same conditions. The gold(I) complex was slowly affected by water. In diethyl ether or tetrachloroethane solution, treatment with water led to decomposition with formation of a deeply colored precipitate (presumably metallic gold). Anal. Calcd for $C_7H_{10}AuCl$: C, 25.7; H, 3.1; Cl, 10.9. Found: C, 25.6, 26.2; H, 2.9, 3.1; Cl, 10.7.

The *cis*-cyclooctene complex was obtained by treating a toluene/dichloromethane suspension of AuCl(CO) with an excess of a 9:1 mixture of *cis*- and *trans*-cyclooctene at about –30 °C. Anal. Calcd for $C_8H_{14}AuCl$: C, 28.0; H, 4.1; Cl, 10.3. Found: C, 28.1; H, 4.3; Cl, 10.0. When the preparation was carried out in *sym*-tetrachloroethane, the complex crystallized out with about 1 mol of $C_2H_2Cl_4$, corresponding to the analytical composition AuCl-(C_8H_{14})·$C_2H_2Cl_4$. Anal. Calcd for $C_{10}H_{16}AuCl_5$: Cl, 34.7. Found: Cl, 34.6. The crystals of this compound collapsed to a colorless

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powder of approximate analytical composition AuCl(C$_8$H$_{14}$) (Anal. Found: C, 27.8; H, 4.7; Cl, 9.2) under reduced pressure at room temperature during the drying procedure. A gas chromatographic analysis (silicon column OV 17, temperature program 30–180 °C, 10°/min, FID) of the products obtained by decomposition of AuCl(C$_8$H$_{14}$)·C$_2$H$_2$Cl$_4$ at room temperature showed the presence of *cis*-C$_8$H$_{14}$ and *sym*-tetrachloroethane, while no *trans*-C$_8$H$_{14}$ could be detected. The IR spectrum of the complex in *sym*-tetrachloroethane showed a band at 1525 cm^{-1} due to the complexed olefinic C–C bond (the uncomplexed olefin has[5] the corresponding band at 1648 cm^{-1}).

Gas Volumetric Study of the AuCl(CO) ⇌ AuCl(olefin) Interconversion. In view of the extreme sensitivity of AuCl(CO) to moisture and in order to minimize the experimental errors in the determination of the equilibrium constant, the following experimental procedure was used. An exactly known amount (about 0.2 g) of AuCl(CO) for each run was introduced in a gas volumetric apparatus; after thermal equilibrium had been reached, a known volume of tetrachloroethane (about 10 cm^3) presaturated with CO was introduced into the reactor from a graduated dropping funnel. The volume difference (volume expansion read on the burette – volume of solvent introduced), if any, was assigned to decomposition of the gold complex due to adventitious presence of moisture. The initial concentration of the gold(I) complex was thus evaluated. The required amount of olefin from the graduated dropping funnel was then introduced into the reactor as a concentrated solution in the same solvent presaturated with CO. The solubility of CO in the solvent and the equilibrium concentrations of reagents and products (the latter calculated from the measured volume of CO evolved after addition of the olefin) were used to obtain an estimate of the equilibrium constant of reaction 1. Unless otherwise stated, the gas volumetric measurements were carried out at the temperature of 21.5 ± 0.1 °C. When the equilibrium was reached, the resulting solution was examined spectrophotometrically and the concentration of the residual AuCl(CO) was determined from the absorbance of the band at 2163 cm^{-1} and compared with that calculated from the gas volumetric measurement. Usually the agreement was very good. Equilibrium 1 was also measured from the direction of the olefin complex through the value of the CO absorbed by the latter. In this case, a known amount of the olefin complex contained in a sealed thin-walled flask was contacted with CO in the same solvent. The volume of CO evolved or absorbed in the two sets of experiments, respectively, was used to calculate the equilibrium constant of the reaction, after correction for the vapor pressure of the solvent.[6] The solubility of CO in tetrachloroethane, not reported in the literature, was determined by the method previously described[1j] and found to be as follows (concentrations expressed as molarity referred to 1 atm of CO (temperature, °C)): 4.7 × 10^{-3} (21.6); 4.6 × 10^{-3} (23.2); 5.0 × 10^{-3} (30.2); 5.2 × 10^{-3} (37.8); 5.2 × 10^{-3} (40.3). The reported solubility of CO[6b] in 1,2-dibromoethane, expressed as the Bunsen coefficient, is 0.078 cm^3 of CO/unit volume of solvent at 25.0 °C, corresponding to a 3.5 × 10^{-3} M concentration.

X-ray Data Collection, Solution, and Refinement of the Structures. (A) AuCl(*cis*-cyclooctene) (AuCl(C$_8$H$_{14}$)). The compound crystallizes as colorless plates from solution in the course of the reaction carried out in dichloromethane/toluene. Approximate cell dimensions, the crystal system, and the systematic extinctions were obtained at –60 °C by using Bürger precession photographs and Mo Kα radiation. The cell dimensions (Table I) have then been refined on an Enraf-Nonius CAD-4 diffractometer with 25 precisely centered high-angle reflections. All experiments on the diffractometer were performed at –80 °C with a crystal of approximate dimensions 0.5 × 0.5 × 0.1 mm^3. In addition to a normal *Lp* correction, the intensities were corrected by using the program DECAY[7] and three standard reflections, as the crystal slowly decomposed during data collection. Averaging the 3003 measured intensities yielded 935 independent reflections

Table I. Summary of Crystal Data and Parameters of the Data Collection and Refinement for AuCl(*cis*-cyclooctene) (1)

formula	AuCl(C$_8$H$_{14}$)
mol wt	342.6
cryst. system	orthorhombic
a, Å	23.115 (4)
b, Å	5.419 (3)
c, Å	7.356 (2)
U, Å^3	921.3
Z	4
space group	$Pca2_1$
D_{cald}, g cm^{-3}	3.100
temp, °C	–80
radiatn (graphite monochromator)	Mo Kα
abs coeff, μ, cm^{-1}	168.6
θ range, deg	3–30
scan type	$^\omega/_\theta$
hkl collected	$0 < h < 7$, $0 < k < 32$, $-10 < l < 10$
measd reflcns	3003
independent reflcns with $I > 3\sigma(I)$	935
no. of variables	51
R	0.037
$R_w{}^a$	0.040

$^a w = 1/\sigma^2$.

Table II. Positional Parameters and Their Estimated Standard Deviations of AuCl(*cis*-cyclooctene)^a

atom	x	y	z	B, Å^2
Au	0.23285 (2)	0.8620 (1)	0.000	2.724 (8)
Cl	0.2980 (2)	0.5484 (6)	–0.004 (2)	3.05 (6)
C(1)	0.1763 (6)	1.152 (3)	–0.091 (2)	1.7 (2)*
C(2)	0.1689 (8)	1.139 (4)	0.095 (3)	2.7 (3)*
C(3)	0.1228 (8)	1.072 (4)	0.209 (3)	3.0 (4)*
C(4)	0.0760 (8)	1.200 (3)	0.238 (3)	2.8 (3)*
C(5)	0.0355 (8)	1.244 (4)	0.074 (3)	3.0 (3)*
C(6)	0.0613 (8)	1.398 (4)	–0.078 (3)	3.4 (4)*
C(7)	0.0807 (8)	1.272 (3)	–0.249 (3)	2.6 (3)*
C(8)	0.1266 (7)	1.025 (3)	–0.213 (3)	2.3 (3)*

^{a} Atoms with an asterisk were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $B_{eq} = {}^4/_3(a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos \gamma)B_{12} + ac(\cos \beta)B_{13} + bc(\cos \alpha)B_{23})$.

with $I > 3\sigma$ (I) and an agreement factor of 0.065. The coordinates of the gold atom could be calculated[7] from the Harker symmetry of a Patterson function. At this stage, the centrosymmetric space group $Pcam$ with Au and Cl located at the mirror plane was assumed and used for completion of the structure with difference Fourier synthesis and refinement with isotropic temperature factors. An absorption correction was then applied by the DIFABS method.[8a] Further refinement with anisotropic temperature coefficients for the gold and chlorine atoms gave $R = 0.049$. Three of the C atoms showed normal B values between 2.4 and 3.9 Å^2. However, the temperature factor of C(5/6) was $B = 12.7$ Å^2 and the two highest peaks in the difference Fourier map were close to C(5/6). A refinement was therefore performed by using these peaks at split positions C(5) and C(6). The B values for these atoms became 3.1 and 2.9 Å^2, with $R = 0.041$, and the difference Fourier map showed no significant electron density at the original position of C(5/6). An ordered model in the noncentrosymmetric space group $Pca2_1$ was then assumed and successfully refined to $R = 0.040$. A difference Fourier synthesis contained no significant electron density in the alternative positions of C(5) and C(6) generated by the mirror plane of the higher symmetry space group $Pcam$. The space group $Pca2_1$ was therefore accepted as the most

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probable, especially since the conformation of the cyclooctene is not compatible with a mirror plane whose existence would imply a disordered structure. A refinement with anisotropic temperature factors for the carbon atoms was attempted, but it resulted in nonpositive coefficients for C(8). In the final refinement, anisotropic temperature coefficients for the Au and Cl atoms only and an extinction coefficient were included. With the calculated coordinates of the H atoms and scattering factors and dispersion correction[8b] for the neutral atoms, the final R value was 0.037. The highest peaks in the difference Fourier map were 2.0 and 1.9 e/Å³, 1.54 and 1.53 Å away from the gold atom. A summary of crystal data and data collection parameters is given in Table I. Atomic coordinates are given in Table II.

(B) AuCl(norbornene) (AuCl(C₇H₁₀)). Suitable crystals of AuCl(C₇H₁₀) as thin colorless platelets were obtained when the preparation was carried out in dichloromethane. One triangular platelet with edges of 0.35, 0.50, and 0.75 mm and a thickness of 0.04 mm was used for the X-ray experiment. The procedure for the determination of the crystal data was the same as for AuCl(C₈H₁₄), starting with precession photographs at –60 °C and continuing with the CAD-4 diffractometer, including data collection at –80 °C. The crystal data are as follows: a = 5.697 (2) Å, b = 20.24 (1), c = 6.620 (2) Å, Z = 4, space group $Ama2$. A correction for the absorption using the ψ-scan method and the EAC program[8c] was applied for the intensities. The shape of the crystal caused minimum and maximum transmission factors of 14.9 and 99.8%, respectively. Consequently, the refinement of the structure did not result in a satisfactory molecular geometry and unreasonable C–C bond lengths were obtained. However, the main feature of the coordination geometry with the expected linear coordination of gold(I) by the chlorine and norbornene ligands was clearly established.

Results and Discussion

Olefin complexes of gold(I) have been reported earlier in the literature,[5] being obtained by the reaction of the olefin with either aqueous tetrachloroauric acid or gold(I) chloride in dry diethyl ether. Apparently, the two methods of preparation gave compounds[5] with consistent analytical data but different decomposition temperatures and crystalline morphology. In our hands, the olefin complexes of gold(I), prepared from AuCl(CO) according to the displacement reaction of eq 1, had to be handled under ex-

$$\text{AuCl(CO)} + \text{olefin} \rightleftharpoons \text{AuCl(olefin)} + \text{CO} \qquad (1)$$

clusion of moisture in order to avoid extensive decomposition. Reaction 1 appears to be the most appropriate method of preparation of the olefin complexes of gold(I) available until now. In fact, in view of the ready availability of anhydrous AuCl₃ by the tetrachloroauric acid–SOCl₂ method,[1a] AuCl(olefin) can be obtained directly from AuCl₃ in dichloromethane via the intermediate in situ reduction to AuCl(CO), prior to the addition of the olefin. Equilibrium 1 is largely shifted to the right (vide infra), which is, of course, helpful from a preparative point of view. It is to be noted that the alternative route to the olefin complexes from AuCl may present some difficulties since AuCl is rarely obtained pure,[10] being metastable with respect to disproportionation to AuCl₃ and Au.[11]

In view of the rather limited information available in the literature about gold(I) olefin complexes, it was decided to solve the structure of the two complexes by X-ray diffraction methods. For minimization of crystal decay during data collection and thermal motion, the data were measured at –80 °C. In view of the low stability of the crystals, the solution of the structure encountered some difficulties and the accuracy of the data, especially for
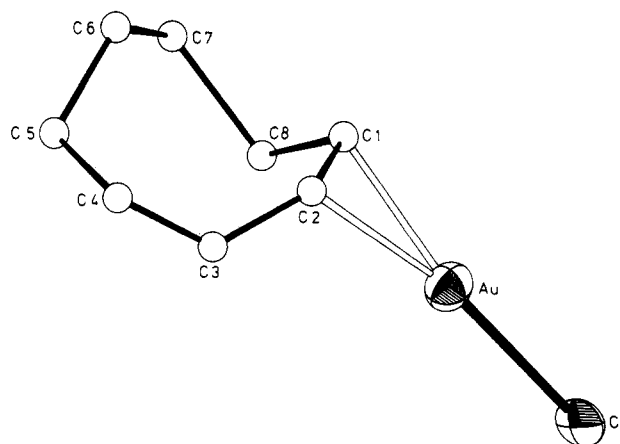

Figure 1. View of AuCl(*cis*-cyclooctene) showing the numbering scheme used.

Table III. Relevant Bond Distances[a] (Å), Nonbonding Distances (Å), and Bond Angles[b] (deg) for AuCl(*cis*-cyclooctene)

Bond Distances			
Au–Cl	2.266 (4)	Au–olefin[c]	2.07 (2)
Au–C(1)	2.15 (2)	C(1)–C(2)	1.38 (2)
Au–C(2)	2.21 (2)	Au···Au	3.758 (1)
Bond Angles			
C(1)–Au–Cl	160.9 (5)	Au–C(1)–C(2)	74 (1)
C(2)–Au–Cl	162.2 (6)	Au–C(2)–C(1)	69 (1)
Olefin–Au–Cl[d]	179.2 (6)	Au–C(1)–C(8)	107 (1)
C(1)–Au–C(2)	36.9 (6)	Au–C(2)–C(3)	121 (1)

[a]Bond distances (Å) within cyclooctene: C(1)–C(8), 1.60 (2); C(7)–C(8), 1.73 (3); C(6)–C(7), 1.50 (3); C(5)–C(6), 1.51 (3); C(4)–C(5), 1.54 (3); C(3)–C(4), 1.30 (3); C(2)–C(3), 1.40 (3). [b]Bond angles (deg) within cyclooctene: C(1)–C(2)–C(3), 134 (2); C(2)–C(1)–C(8), 116 (1); C(1)–C(8)–C(7), 101 (1); C(6)–C(7)–C(8), 114 (2); C(5)–C(6)–C(7), 119 (2); C(4)–C(5)–C(6), 115 (2); C(3)–C(4)–C(5), 117 (2); C(2)–C(3)–C(4), 126 (2). [c]Au–center of the CC bond distance. [d]Angle at the gold atom with the vector connecting center of the CC bond.

AuCl(norbornene), is low. However, the data are of sufficient quality to establish the main features of the coordination geometry. The two complexes exhibit the expected linear geometry by considering the olefin as occupying one coordination site; see the structure of 1 in Figure 1. As a consequence of the low accuracy of the structure determination of 2, detailed data are not given for this compound.

In 1, the angle at gold between the Au–Cl bond and the vector connecting the gold atom with the center of the C–C olefinic bond does not deviate substantially from 180°; see Table III. The Au–Cl distance in the complex is 2.266 (4) Å, thus substantially identical, within experimental error, with the value of 2.261 (6) Å found[4] in AuCl(CO) and similar to other values observed[12] in several complexes of AuCl. A literature survey has shown that apparently no X-ray studies of metal complexes of *cis*-cyclooctene have been made with the unique exception of Rh₂Cl₂(*cis*-C₈H₁₄)₂(PMe(SiMe₃)₂)₂,[12b] in which the C–C bond distance of the coordinated ligand was found to be 1.413 (4) Å. The C–C bond distance of the coordinated olefin in 1 (1.38 (2) Å) is the same within experimental error. Generally, coordination of olefins to metals is accompanied by a small increase of the C–C bond distance.[13] The C–C bond distance of *trans*-cyclooctene, as determined by gas-phase

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Table IV. IR Vibrations (cm⁻¹) of AuCl(*cis*-cyclooctene) and AuCl(norbornene)

assignment	AuCl(*cis*-cyclooctene)	AuCl(norbornene)
ν(CC)	1525 w[a]	1440 w[a]
ν_s(AuCC)	540 w[b]	552 m[b]
ν_{as}(AuCC)	516 s[b]	531 m[b]
ν(AuCl)	337 s[b]	327 s[b]
δ(ClAuC)	78 s[b]	78 s[b]

[a] Tetrachloroethane solution in CaF₂ cells. This is the most intense band in this region. For the norbornene complex, other bands were observed at 1480 w (sh), 1450 m, and 1420 w cm⁻¹. The IR spectrum as (C₂Cl₃F)ₙ mull has the bands specified in the Experimental Section. By comparison with the spectra of uncomplexed olefin and on the basis of the intensity, the 1440 cm⁻¹ band has been assigned to the CC stretching vibration in the complex. [b] Polyethylene pellets.

electron diffraction,[14] is 1.332 (17) Å. The value of 1.38 Å found for our *cis*-cyclooctene gold complex is therefore well within the range of values normally encountered in olefin complexes of univalent cations and substantially identical with the C–C bond distance found[15] in [Mn-(CO)₅C₂H₄]⁺ (1.376 Å) and in Rh₂Cl₂(C₂H₄)₄ (1.376 Å).

The present study has established that the structure consists of discrete AuCl(olefin) molecules. The crystal packing of these complexes exhibits the closest nonbonding Au···Au distance of 3.758 (1) Å, to be compared with the value of 3.38 Å observed in AuCl(CO).[4] The Au–Au distance in the metal[16] is 2.884 Å. We can thus conclude that no important intermetallic contacts were present in the olefin complex.

The IR data of the olefin complexes are given in Table IV. As expected, the C=C stretching vibration of coordinated olefin was observed at a considerably lower value in comparison with the corresponding uncomplexed olefin (1648 cm⁻¹ for *cis*-cyclooctene[13] and 1568 cm⁻¹ for norbornene[13]). The Au–Cl stretching vibrations are in the usual range for complexes of the type AuCl(L), such as AuCl(CO), 360 cm⁻¹, AuCl(PPh₃),[17] 329 cm⁻¹, and Au-Cl₂⁻,[18-20] 332–350 cm⁻¹. In the far-IR region, absorptions were observed at 78 cm⁻¹ assigned to a Cl–Au–C bending vibration (AuCl(CO) has a similar vibration at 91 cm⁻¹).

No studies appear to have been published on the competitive coordinative ability of CO and olefins for noble metals (palladium, platinum, silver, and gold). Our data on the displacement reaction 1 are therefore relevant to assess this specific point for gold(I). The constant for equilibrium 1 (olefin = norbornene) is $K = 4 \pm 1$ at 21.5 °C, thus showing that the $\Delta G°$ for the reaction is about 1 kcal/mol of olefin complex. In view of the numerous difficulties connected with the low stability of the system, it was not possible to establish conclusively the enthalpy and entropy contributions by measuring the equilibrium constants at different temperatures. It was possible to establish, however, that equilibrium 1 is not greatly affected by temperature in the 0–4C °C range, thus implying a relatively small value of $\Delta H°$. It is, on the other hand, remarkable that reaction 1 can be proposed as a preparative method for the olefin complexes. Usually, for typical transition-metal cations, the opposite is true, and CO

displaces the coordinated olefin from the complex. Cramer[21] in a study of the olefin displacement by CO from Rh(acac)(C₂H₄)₂ found that the constant of the substitution equilibrium was above 100, thus showing that the carbonyl complex was largely favored with respect to olefin coordination, in spite of the presumably unfavorable entropy change. Markó and co-workers[22] recently found that the displacement of CO in Co₂(CO)₈ by norbornadiene (NBD) to give Co₂(CO)₆(NBD) did occur to a small extent, the equilibrium constant for the formation of the diolefin complex being $(6.7 \pm 0.4) \times 10^{-4}$ M at 35 °C. Also photochemically generated[23a] Cr(CO)₅(*cis*-cyclooctene) reacts with ¹³CO to give Cr(CO)₅(¹³CO). Mention has also been made of the fact, however, that the CO ligand can be displaced by olefins in the pyrazolylborato complex of copper(I), Cu(HB(pz)₃)CO.[23b] It therefore appears that on moving toward the end of the transition series within the domain of the noble metals, coordination of the olefins to the central metal atom may become favorable with respect to CO; the dominating factor may be entropic. The enthalpy change connected with the complexation of olefins to solid silver fluoborate was found to be between 9 and 13 kcal/mol.[24] It is interesting to note that, while complexation of *cis*-cyclooctene and norbornene occurs promptly with AuCl(CO), no CO displacement was observed with either acrylonitrile or tetracyanoethylene. Styrene displaced CO from AuCl(CO), but no pure compound could be obtained, probably because of the low stability of the olefin complex in the solid state. The failure of the olefins containing electron-withdrawing cyano groups to coordinate to gold(I) is consistent with the data obtained[25] with palladium(II), showing that complexation was favorable for olefins containing ring substituents with π-donating ability. On the other hand, the easier isolation of olefin complexes of iridium(I) with electron-withdrawing cyano substituents has been attributed to an intrinsic overall stronger metal–olefin bond as a consequence of a better overlap between filled metal orbitals and π^* orbitals of the olefin.[26] However, as mentioned earlier, an important π-back-bonding contribution in Zeise's salt, [PtCl₃(C₂H₄)]⁻, has recently been questioned.[2] Olefin complexes of silver(I) had been already recognized[21,27] to result from a prevailing σ contribution to the bond, and our data on gold(I) appear to be in agreement with the latter assumption.

Supplementary Material Available: Listings of anisotropic temperature coefficients for the Au and Cl atoms (1 page); listings of structure factor amplitudes (22 pages). Ordering information is given in any current masthead page.

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