

[cis- $\{\eta^2-(\text{Ph}_3\text{PAu})_2\}\text{Ph}_3\text{PCr}(\text{CO})_4\} \cdot \text{THF}$, featuring the shortest known separation between two Au metal centres in a heteronuclear Au_2M cluster

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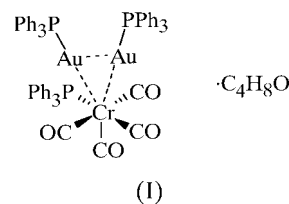
The title compound, tetracarbonyl-1 κ^4 C-tris(triphenylphosphino)-1 κ P,2 κ P,3 κ P-triangulo-chromiumdigold(Au–Au)-(2 Cr–Au) tetrahydrofuran solvate, $[\text{Au}_2\text{Cr}(\text{C}_{18}\text{H}_{15}\text{P})_3(\text{CO})_4] \cdot \text{C}_4\text{H}_8\text{O}$, is a stable isolobal analogue of the extremely labile $[(\eta^2\text{-H}_2)\text{Cr}L_{n-1}]$ molecular hydrogen complex ($n = 6$; L is a neutral ligand, e.g. CO or PPh_3), and features the shortest known separation [2.6937 (2) Å] between two Au atoms in a triangular heteronuclear metal-cluster framework.

Comment

Triangular metal-cluster compounds are of manifold interest as a result of their interesting metal–metal bonding modes and their application as catalysts or catalyst precursors (Pignolet & Krogstad, 1999). In particular, cluster complexes containing Au atoms have received a lot of attention because of the frequent occurrence of Au–Au aurophilic interactions in such compounds (Pyykkö, 1988). Early work by Lewis and Nyholm (Coffey *et al.*, 1964) paved the way for the systematic synthesis of heteronuclear cluster complexes containing Au atoms, and many structurally characterized examples, exhibiting a variety of gold–metal ratios, are known today (Pignolet & Krogstad, 1999). Stone *et al.* (Green *et al.*, 1982) demonstrated the use of transition metal hydrides in the synthesis of the first bimetallic chromium–gold compounds when they prepared $[(\text{Ph}_3\text{PAu})(\mu\text{-H})\text{Cr}(\text{CO})_5]$. This complex provided both a rare example of a hydride complex of gold and an isolobal model for the unstable $[(\eta^2\text{-H}_2)\text{Cr}(\text{CO})_5]$ molecular hydrogen complex (Green *et al.*, 1982; Sweany, 1985; Sweany & Moroz, 1989). However, the analogous η^2 -digold–Cr(CO)₅ complex has never been reported. The title complex, (I), which is reported here, is therefore the first example of a η^2 -digold complex with chromium. The closest structurally characterized analogue to

(I) is the cationic $[\eta^2-(\text{Ph}_3\text{PAu})_2\text{PMe}_3\text{MoCp}(\text{CO})_2]$ complex reported by Gallasi *et al.* (1997).

In the course of our investigations into the electrophilic addition of Ph_3PAu^+ to anionic Fischer-type carbene complexes (Raubenheimer *et al.*, 2002), we isolated (I) as a brightly coloured by-product of the reaction between N -deprotonated Fischer-type aminocarbene complexes and Ph_3PAuCl . Low-temperature (258 K) silica-gel chromatographic separation of the crude reaction mixture revealed (I) as a bright-red polar band, which could be eluted from the column with tetrahydrofuran (THF). Crystallization from THF layered with n -pentane yielded the pure compound (yield up to 10%). Complex (I) is soluble in polar organic solvents (such as THF, CH_2Cl_2 and CHCl_3), insoluble in non-polar solvents (such as n -pentane and n -hexane), and moderately sensitive to air and moisture. However, in the solid state, (I) can be stored at freezer temperatures under an atmosphere of dry argon for prolonged periods.



The molecular structure of (I) (Fig. 1) exhibits a $\text{PPh}_3\text{Cr}(\text{CO})_4$ fragment in a pseudo-octahedral configuration, with two Ph_3PAu fragments interacting with the central Cr atom and with one another, thus filling the sixth coordination position on the Cr atom and forming a trinuclear triangular CrAu_2 metal-cluster centre. This bonding mode of the two Ph_3PAu fragments to a neutral metal centre has also been described as a three-centre two-electron system, in which the $\text{PPh}_3\text{Au}-\text{AuPPh}_3$ grouping is regarded as a single η^2 - $(\text{AuPPh}_3)_2$ 'ligand' (Hall & Mingos, 1984). This description of the metal–metal bonding in (I) relates the current complex to the extremely labile isolobal $[(\eta^2\text{-H}_2)(\text{P}^i\text{Pr}_3)_2\text{Cr}(\text{CO})_3]$ complex (Kubas *et al.*, 1994).

The metal–metal separations and bond angles within the trimetallo-cyclopropane ring in (I) show an almost perfect equilateral triangle [Au1–Cr = 2.6932 (6) Å, Au2–Cr = 2.7038 (7) Å, Au1–Au2 = 2.6937 (2) Å, Au1–Cr–Au2 = 59.881 (15)°, Cr–Au1–Au2 = 60.254 (16)° and Cr–Au2–Au1 = 59.865 (15)°; Table 1]. Of greatest interest here is the Au1–Au2 distance, which is the shortest known crystallographically determined separation between two Au^I centres in a hetero-trinuclear cluster compound. Slightly shorter Au–Au separations have been reported for gold cluster compounds in which three or more Au atoms are linked to one another, but the bonding situation in such compounds is difficult to describe (Cheetham *et al.*, 1993; Gabbai *et al.*, 1995). The Au1–Au2 distance in (I) is 0.1903 (2) Å shorter than that in metallic gold (2.884 Å; Jones, 1983) and is thus clearly within bonding distance [the sum of the van der Waals radii for two Au atoms is 3.32 Å (Jones, 1981)]. This result

supports our description of (I) as $[\{\eta^2\text{-(AuPPh}_3)_2\}\text{PPh}_3\text{Cr(CO)}_4]$.

The shortening of Au–Au distances in triangular MAu_2 cluster compounds has been linked to the electron density at the metal centre, M (Gallasi *et al.*, 1997). A higher electron density on M corresponds to better interaction with electrophilic Ph_3PAu fragments and also decreases the $\text{Au}^{\delta+}\text{--Au}^{\delta+}$ repulsion. Thus, the electron density on the Au atoms effectively increases and the Au–Au aurophilic interaction is strengthened to a point where the Au_2 configuration in the MAu_2 cluster can be formally regarded as an Au–Au σ -bond coordinated to the neutral metal centre, M . The presence of an excellent σ -donating PPh_3 ligand in (I) is consistent with an increase in the electron density on the Cr atom, thus reinforcing our explanation for the extremely short Au–Au separation observed in this compound. The P–Cr bond [Cr–P3 = 2.3986 (12) Å] is significantly longer than that in other structurally characterized $[\text{R}_3\text{PCr(CO)}_5]$ complexes (Affandi *et al.*, 1988; Hengefeld *et al.*, 1983; Lee & Brown, 1992). This fact, together with the downfield-shifted ^{31}P NMR resonance for this P atom and the relatively low frequency at which the CO stretching frequencies in (I) appear, as discussed below, also supports our interpretation of the metal–metal bonding mode in (I). A C4–C3–Au1–Au2 torsion angle of 29.19 (8) $^\circ$ describes how the $\eta^2\text{-(AuPPh}_3)_2$ 'ligand' is orientated relative to the $\text{PPh}_3\text{Cr(CO)}_3$ coordination plane. Distortion of this coordination plane is described by deviations of -0.0240 (16), -0.023 (2), 0.032 (2), 0.032 (2) and -0.0167 (15) Å, respectively, from the least-squares plane through atoms Cr, C2, C3, C4 and P3. An angle of 86.91 (6) $^\circ$ describes the orientation of the Cr–Au1–Au2 triangle relative to the least-squares mean plane through atoms Cr, C2, C3, C4 and P3.

The Cr–Au1–P1 and Cr–Au2–P2 angles of 168.12 (4) and 169.74 (3) $^\circ$ reflect the distortion of the normally linear Au^{I} coordination due to the strong Au–Au interaction, which draws the Au atoms into closer proximity with each other

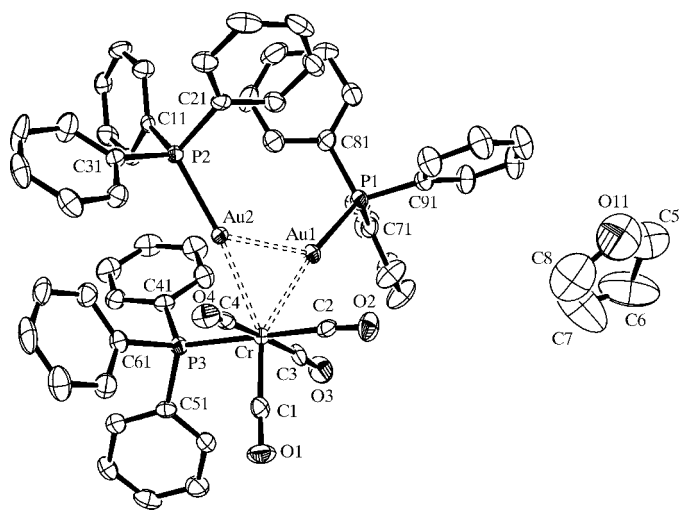


Figure 1
ORTEP-3 (Farrugia, 1997) plot of (I), showing the atom-numbering scheme and displacement ellipsoids at the 50% probability level. H atoms have been omitted for clarity.

while the bulky PPh_3 ligands are unable to form such a tight fit. Furthermore, the three PPh_3 ligands in (I) rotate so as to minimize the steric hindrance with one another and with the CO ligands; the staggered PPh_3 conformations are indicated by the C91–P1–Cr–P3 [178.20 (18) $^\circ$], C21–P2–Cr–P3 [171.33 (14) $^\circ$] and C81–P1–P2–C31 [179.7 (5) $^\circ$] torsion angles.

In the crystal structure, molecules of (I) pack together with an uncoordinated and slightly disordered THF solvent molecule (Fig. 1). All attempts to model this disorder were unsuccessful, as it appears to be the result of a combination of dynamic and static effects. There are no significant intermolecular interactions present in the lattice of (I).

The IR spectrum of (I) was recorded as a KBr pellet. The C_{2v} local symmetry about the metal in complexes of the type $[\text{cis-}L_2M(\text{CO})_4]$ (where L is a neutral ligand, *e.g.* CO or PPh_3) allows for four IR-active vibrational modes in the carbonyl region ($2 \times A_1$, B_1 and B_2). All four of these were clearly visible in the IR spectrum of (I), where they appeared at relatively low frequencies compared with those observed for other reported chromium carbonyl compounds (Raubenheimer *et al.*, 2002). This shift to lower energy is ascribed both to efficient electron donation from the PPh_3 ligand coordinated to the Cr atom in (I), which increases the electron density on this atom, and to the back-donation of electrons to the CO and AuPPh_3 fragments. This electron density is believed to play an important role in cancelling out $\text{Au}^{\delta+}\text{--Au}^{\delta+}$ repulsive effects between the two Ph_3PAu fragments, which allows the Au centres to interact more effectively and explains the extremely short Au–Au separation found in (I).

Experimental

All reactions and manipulations were carried out under a dry argon atmosphere using standard Schlenk and vacuum-line techniques. All solvents were dried and purified by conventional methods and were freshly distilled under argon shortly before use. Melting points were measured with a Büchi 535 melting-point determination apparatus and are uncorrected. NMR spectra were recorded on a Varian INOVA 600 spectrometer (^1H , 600 MHz; $^{13}\text{C}\{^1\text{H}\}$, 151 MHz; $^{31}\text{P}\{^1\text{H}\}$, 243 MHz) at 298 K. Chemical shifts are reported in units of p.p.m. relative to residual ^1H and ^{13}C signals from the deuterated solvents. The IR spectra were recorded on a Perkin Elmer 1600 Series FT-IR spectrometer. Elemental analyses were performed on a Fisons CHNS elemental analyser 1108. Ph_3PAuCl and the various Fischer-type aminocarbene complexes were prepared according to published procedures (Fischer & Leopold, 1972). BuLi (*ca.* 1.6 M solution in diethyl ether) was purchased from Merck and standardized before use. For the preparation of (I), a solution of the Fischer-type aryl/alkylaminocarbene complex (0.8 mmol) in THF (15 ml) was slowly reacted at 195 K with BuLi (1 mole equivalent 1.6 M, 0.4 ml). The mixture was stirred for 10 min and then Ph_3PAuCl (395 mg, 0.8 mmol) was added to the solution. The mixture was stirred for 30 min at this temperature and then was allowed to warm to room temperature over a period of 2 h. Removal of the solvent *in vacuo* resulted in dark-yellow–brown oily residues containing a mixture of products (thin-layer chromatography). Purification by column chromatography (SiO_2 , THF) and crystallization from THF/*n*-pentane

yielded bright-red crystals of (I) [yield up to 108 mg, 10%; m.p. 440 K (decomposition)]. NMR (CD₂Cl₂) ¹H: 6.9–7.7 (*m*, 45H, Ph); ¹³C{¹H}: 129.0 [*t*, ²J_{CP} = 3.3 Hz, PhC(*ortho*)], 132.4 [*t*, ¹J_{CP} = 22.9 Hz, PhC(*ipso*)], 134.4 [*t*, ³J_{CP} = 4.8 Hz, PhC(*meta*)], 130.8 [*s*, PhC(*para*)], 231.5 [*d*, ²J_{PC} = 9.9 Hz, CO(*cis*)], 233.9 [*d*, ²J_{PC} = 18.3 Hz, CO(*trans*)]; ³¹P{¹H}: 50.9 (*d*, ³J_{PP} = 5.4 Hz, 2P, Ph₃PAu), 71.5 (*d*, ³J_{PP} = 5.3 Hz, 1P, Ph₃PCr); IR (KBr): ν(CO) 1839 (*s*), 1864 (*s*), 1942 (*s*), 2004 cm⁻¹ (*w*). Analysis calculated for C₅₈H₄₅Au₂CrO₄P₃ (1344.84 g mol⁻¹): C 51.80, H 3.37, O 4.76%; found: C 52.05, H 3.43, O 4.82%. Crystals of (I) suitable for single-crystal X-ray diffraction analysis were obtained by recrystallization from THF/*n*-pentane.

Crystal data

[Au₂Cr(C₁₈H₁₅P₃(CO)₄)]₂·C₄H₈O
M_r = 1417.01
 Triclinic, *P* $\bar{1}$
a = 11.4841 (2) Å
b = 13.5642 (3) Å
c = 17.5171 (4) Å
 α = 87.147 (1)°
 β = 88.062 (1)°
 γ = 81.073 (1)°
V = 2691.35 (10) Å³
Z = 2
D_x = 1.748 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 5717 reflections
 θ = 1.0–27.5°
 μ = 5.78 mm⁻¹
T = 173 (2) K
 Monoclinic prism, red
 0.35 × 0.27 × 0.17 mm

Data collection

Nonius KappaCCD diffractometer
 φ and ω scans
 Absorption correction: empirical (DENZO-SMN; Otwinowski & Minor, 1997)
T_{min} = 0.169, *T_{max}* = 0.375
 14 365 measured reflections
 10 345 independent reflections
 7951 reflections with *I* > 2σ(*I*)
R_{int} = 0.025
 θ_{max} = 26.0°
h = -14 → 14
k = -13 → 16
l = -21 → 21

Table 1

Selected geometric parameters (Å, °).

C1—O1	1.171 (5)	C4—Cr	1.887 (5)
C1—Cr	1.829 (5)	C4—Au2	2.564 (4)
C2—O2	1.165 (4)	Au1—P1	2.2854 (11)
C2—Cr	1.853 (4)	Au1—Cr	2.6932 (6)
C3—O3	1.147 (5)	Au1—Au2	2.6937 (2)
C3—Cr	1.899 (5)	Au2—P2	2.3022 (12)
C3—Au1	2.621 (5)	Au2—Cr	2.7038 (7)
C4—O4	1.162 (5)	P3—Cr	2.3986 (12)
O1—C1—Cr	175.6 (4)	C1—Cr—Au1	150.29 (15)
O2—C2—Cr	175.4 (4)	C2—Cr—Au1	73.89 (13)
O3—C3—Cr	174.5 (4)	C4—Cr—Au1	115.28 (12)
O4—C4—Cr	171.3 (4)	C3—Cr—Au1	67.04 (13)
P1—Au1—Cr	168.12 (4)	P3—Cr—Au1	106.77 (3)
P1—Au1—Au2	130.12 (3)	C1—Cr—Au2	148.92 (15)
Cr—Au1—Au2	60.254 (16)	C2—Cr—Au2	101.20 (13)
P2—Au2—Au1	129.75 (3)	C4—Cr—Au2	65.08 (13)
P2—Au2—Cr	169.74 (3)	C3—Cr—Au2	118.86 (14)
Au1—Au2—Cr	59.865 (15)	P3—Cr—Au2	78.46 (3)
C4—Cr—C3	175.63 (19)	Au1—Cr—Au2	59.881 (15)
C2—Cr—P3	178.88 (14)		

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.031
wR(*F*²) = 0.057
S = 0.99
 10345 reflections
 658 parameters
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0107P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 1.13 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{min} = -0.98 \text{ e } \text{Å}^{-3}$

Although it was possible to locate most of the H atoms in (I) from a Fourier map, all H atoms were placed in idealized positions [aryl C—H = 0.95 Å, methylene C—H = 0.99 Å and *U*_{iso}(H) = 1.2*U*_{eq}(C)].

Data collection: COLLECT (Nonius, 1999); cell refinement: DENZO-SMN (Otwinowski & Minor, 1997); data reduction: DENZO-SMN; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: WinGX (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1531). Services for accessing these data are described at the back of the journal.

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