

"Aurolysis of α -C-deprotonated group 6 aminocarbene and thiocarbene complexes with Ph_3PAu^+ "; H. G. Raubenheimer, M.W. Esterhuysen, G. Frenking, A. Y. Timoshkin, C. Esterhuysen and U.E.I. Horvath

Disorder 7/7'

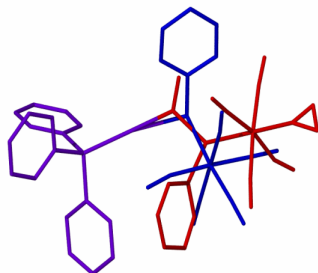


Fig. S1 View showing disorder in 7/7'. For clarity Hs and full site occupancy molecule of 7 have been omitted. Red=7, blue =7', purple=atoms common to both 7 and 7'.

Preparation and analysis of pure 7'

General

Reactions were carried out under argon using standard Schlenk and vacuum-line techniques. All solvents were dried according to standard literature methods.ⁱ The melting point was determined on a Stuart Scientific Melting Point Apparatus SMP3 and is uncorrected. The mass spectrum was recorded on a VG 70SEQ (FAB, 70 eV) instrument, the infrared spectra on a Nicolet Avatar 330 FT-IR with ATR (attenuated total reflection) accessory (Smart Performer) and NMR spectra on a Varian Unity INOVA 400 MHz spectrometer (δ reported relative to the solvent resonance or external reference, 85% H_3PO_4).

Gold(I) starting material, triphenylphosphinegold chloride,^{ii,iii,iv} was prepared by substitution of tht in $\text{ClAu}^{\text{v,vi}}$ with triphenylphosphine. Comparison of the characterisation data in the literature confirmed the purity of the starting material. All the other chemicals are commercially available and were used without further purification.

Synthesis of (benzenethiolato)(triphenylphosphine)gold^{vii}

The complex was obtained by addition of lithium phenylthiolate (75 mg, 0.65 mmol) to a suspension of triphenylphosphinegold chloride (0.32 g, 0.65 mmol) in thf (20 ml), stirred at $-10\text{ }^\circ\text{C}$. The mixture was allowed to warm up to room temperature and stirred for 4 h. After solvent removal the mixture was treated with CH_2Cl_2 (20 ml), filtered over celite and dried *in vacuo*, to yield colourless, microcrystalline material (0.31 g, 84%).

Synthesis of pentacarbonyl[(benzenethiolato)(triphenylphosphine)gold]chromium(0)

$[(\text{CO})_5\text{Cr}(\text{THF})]$ was generated by irradiation of $\text{Cr}(\text{CO})_6$ (0.13 g, 0.59 mmol) in THF (110 ml) for 2 h at room temperature. The orange solution was transferred *via* canula onto (benzenethiolato)(triphenylphosphine)gold (0.31 g, 0.54 mmol) and stirred for 1 h at room temperature. After solvent removal the residue was dried *in vacuo*, to yield yellow, microcrystalline material (0.25 g, 61%).

M. p. $100\text{ }^\circ\text{C}$ (dec.). (Found: C, 45.80; H, 2.65; S 4.22, $\text{C}_{29}\text{H}_{20}\text{AuCrO}_5\text{PS}$ requires C, 45.41; H, 2.65; S, 4.59%). IR (n-hexane): $\nu = 2062, 1987, 1935, 1926, 1905\text{ cm}^{-1}$. IR (CH_2Cl_2): $\nu = 2060, 1980, 1930, 1889\text{ cm}^{-1}$. IR (ATR): $\nu = 3056$ (w), 2961 (w), 2067 (m, CO), 1977 (w, CO), 1970 (w, CO), 1937 (s, CO), 1917 (s, CO), 1896 (s, CO), 1876 (s, CO), 1576 (w), 1480 (w), 1435 (m), 1260 (w), 1100 (m), 1022 (m), 998 (w), 801 (w), 746 (m), 738 (m), 712 (m), 691 (s), 688 (s), 665 (s), 641 (vs), 617 (m) cm^{-1} . ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 7.56$ (m, 15H, P- C_6H_5), 7.10 (m, 5H, S- C_6H_5). ^{13}C NMR (101 MHz, CD_2Cl_2): $\delta = 223.8$ (*trans*-CO), 216.5 (*cis*-CO), 134.5 (d, $^2\text{J} = 13.9\text{ Hz}$, *meta*-P- C_6H_5), 133.4 (*meta*-S- C_6H_5), 133.3 (d, $^4\text{J} = 2.2\text{ Hz}$, *para*-P- C_6H_5), 129.7 (d, $^3\text{J} = 11.7\text{ Hz}$, *ortho*-P- C_6H_5), 128.9 (*ortho*-S- C_6H_5), 128.8 (d, $^1\text{J} = 58.6\text{ Hz}$, *ipso*-P- C_6H_5), 126.6 (*para*-S- C_6H_5), 123.6 (*ipso*-S- C_6H_5). ^{31}P NMR (162 MHz, CD_2Cl_2): $\delta = 37.1$. FAB-MS: $m/z = [\text{M}^+]$

Crystal structure determination of complex 7'

Crystal data for 7': 2(C₂₉H₂₀AuCrO₅PS), *M* = 1520.89, golden blocks, 0.30 × 0.25 × 0.20 mm³, triclinic, space group P1 (No. 2), *a* = 11.3464(11), *b* = 12.2837(12), *c* = 20.705(2) Å, α = 87.165(2), β = 76.637(2), γ = 76.024(2)°, *V* = 2724.4(5) Å³, *Z* = 4, *D_c* = 1.854 g/cm³, *F*₀₀₀ = 1472, Bruker SMART Apex Diffractometer^{viii}, MoK α radiation, λ = 0.71073 Å, *T* = 173(2)K, 2 θ _{max} = 51.5°, 20464 reflections collected, 10239 unique (*R*_{int} = 0.029). The structure was solved and refined using the programs SHELXS-97 and SHELXL-97^{ix} respectively. The program X-Seed^x was used as an interface to the SHELX programs, and to prepare the figure. Final *Goof* = 1.056, *RI* = 0.036, *wR2* = 0.080, *R* indices based on 8655 reflections with *I* > 2 σ (*I*) (refinement on *F*²), 685 parameters, 0 restraints. Lp^{xi} and absorption corrections^{xii} applied, μ = 5.95 mm⁻¹.

Fig. S2 shows the molecular structure and atom numbering scheme of 7'. The structure consists of dimers of (CO)₅CrS(Ph)AuPPh₃ owing to Au...Au interactions [3.1869(4)Å]. Selected bond lengths and angles are given in Table 1.

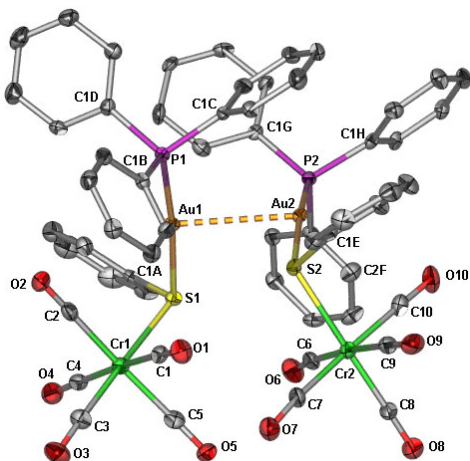


Fig. S2 Ortep view of 7' (hydrogen atoms omitted for clarity), showing the numbering scheme. Ellipsoids are shown at the 50% probability level.

Table 1 Selected bond lengths (Å) and angles (°) with s.u.s in parenthesis for 7'

Au-S	2.328(1),	2.318(2)	S-Au-P	170.42(5),	174.08(5)
S-C	1.790(6),	1.797(6)	Au-S-C	109.1(2),	103.2(2)
S-Cr	2.513(2),	2.514(2)	Au-S-Cr	101.69(6),	100.44(6)
Au-P	2.265(2),	2.260(2)	Cr-S-C	106.2(2),	107.8(2)

ⁱ R. J. Errington, *Advanced Practical Inorganic and Metalorganic Chemistry*, p. 92, Blackie Academic & Professional, London (1997).

ⁱⁱ M. I. Bruce, B. K. Nicholson, O. Bin Shawkataly, in H. D. Kaesz (eds), *Inorg. Synth.* **26**, Wiley, 325 (1989).

ⁱⁱⁱ W. A. Herrmann, A. Salzer, *Synthetic Methods of Organometallic and Inorganic Chemistry* **1**, Thieme Verlag, Herrmann/Brauer, 170 (1996).

^{iv} G. H. Woehrle, L. O. Brown, J. E. Hutchison, *J. Am. Chem. Soc.* **127**, 2172 (2005).

^v A. Hass, J. Helmbrecht, U. Niemann, in G. Brauer (eds), *Handbuch der Präparativen Anorganischen Chemie*, Ferdinand Enke Verlag, Stuttgart, 1014 (1978).

^{vi} R. Uson, A. Laguna, M. Laguna, in H. D. Kaesz (eds), *Inorg. Synth.* **26**, Wiley, 86 (1989).

^{vii} S. Onaka, Y. Katsukawa, M. Shiotsuka, O. Kanegawa, M. Yamashita, *Inorg. Chim. Acta* **312**, 100 (2001).

^{viii} *SMART Data Collection Software*, Version 5.629, Bruker AXS Inc., Madison, WI, 2003.

^{ix} G.M. Sheldrick, *SHELX-97*, Program for crystal structure analysis, University of Göttingen, Germany, 1997.

^x L.J. Barbour, *J. Supramol. Chem.*, 2001, **1**, 189.

^{xi} *SAINT, Data Reduction Software*, Version 6.45, Bruker AXS Inc., Madison, WI, 2003.

^{xii} *SADABS*, Version 2.05, Bruker AXS Inc., Madison, WI, 2003.