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Hydrido-bridged Bimetallic Complexes involving Gold or Silver and Chromium, Molybdenum, or Tungsten: *X*-Ray Crystal Structure of $[AuCr(\mu\text{-}H)(CO)_5(PPh_3)]$ *

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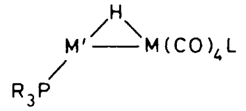
Treatment of tetrahydrofuran solutions of the salts $[N(PPh_3)_2][MH(CO)_4L]$ [M = Cr or W, L = CO; M = W, L = $P(OMe)_3$] with $[AuCl(PPh_3)]$ in the presence of $TlPF_6$ afforded the compounds $[AuM(\mu\text{-}H)(CO)_4L(PPh_3)]$. The gold–molybdenum compound $[AuMo(\mu\text{-}H)(CO)_5(PPh_3)]$ was similarly prepared from a dichloromethane solution of $[N(PPh_3)_2][Mo_2(\mu\text{-}H)(CO)_{10}]$. Reactions between $[N(PPh_3)_2][MH(CO)_4L]$ [M = Cr or W, L = CO; M = W, L = $P(OMe)_3$], $[AgI(PMe_3)]$, and $TlPF_6$ yielded the hydrido-bridged bimetal compounds $[AgM(\mu\text{-}H)(CO)_4L(PMe_3)]$. A single-crystal *X*-ray diffraction study has been carried out on the complex $[AuCr(\mu\text{-}H)(CO)_5(PPh_3)]$. The molecule has a bent Au(μ-H)Cr geometry [Au–Cr 2.770(2), Au–H 1.72(11), and Cr–H 1.64(12) Å; Au–H–Cr 111(5)°] in accord with the presence of a three-centre two-electron bond. The orientation of the $Cr(CO)_5$ group is staggered relative to the Au(μ-H)Cr bridge, with the hydrido-ligand lying *transoid* to the axial carbonyl ligand and the phosphine group. Crystals are triclinic, space group $P\bar{1}$ (no. 2), and the structure has been refined to *R* 0.047 for 3 401 intensities measured at 210 K in the range $4 \leqslant 2\theta \leqslant 50°$. Proton, $^{31}P\text{-}\{^1H\}$, and $^{13}C\text{-}\{H\}$ n.m.r. spectroscopic data for the various compounds are reported and show that these species undergo dynamic behaviour in solution involving dissociation of the PPh_3 or PMe_3 groups, site exchange of CO ligands, and, for the silver-containing complexes, dissociation of the $MH(CO)_4L$ fragments.

In this paper we describe the synthesis of the bimetallic hydrido-bridged compounds (1)—(7), and the structural characterisation of the chromium–gold complex (1) by a single-crystal *X*-ray diffraction study. These compounds contain heteronuclear metal–metal bonds bridged by a single hydrido-ligand, and they were the first species of this kind involving gold or silver to be reported.[1] However, since our preliminary communication appeared, the bimetallic compounds $[AuIrH_2(\mu\text{-}H)(PR_3)(PPh_3)_3][BF_4]$ (R = Et or Ph) and $[AuPt(C_6Cl_5)(\mu\text{-}H)(PEt_3)_3][BF_4]$ have been prepared,[2] thereby adding to this class of complex. The new compounds described herein are directly related to the homo-dinuclear anions $[M_2(\mu\text{-}H)(CO)_{10}]^-$ (M = Cr, Mo, or W), which also contain so-called [3] 'unsupported' M–H–M three-centre two-electron bonds. Prior to the discovery [4–6] of the dimetal species $[M_2(\mu\text{-}H)(CO)_{10}]^-$, and determination of their structures [7] and those of derivatives [8] such as $[Mo_2(\mu\text{-}H)(CO)_9(PPh_3)]^-$, our knowledge of hydrido-bridged 'electron-deficient' bonding had been limited to the boranes, although complexes containing B–H–M (M = Cr, Mn, Zr, *etc.*) linkages were identified [9] at about the same time that definitive work on the dimetal monoanions of the Group 6B metals began.

Few dimetallic compounds with hydrido-ligands bridging heteronuclear metal–metal bonds are known; recent examples include the platinum–tungsten complexes $[PtW(\mu\text{-}H)(\mu\text{-}CHR)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]$ (R = Me or C_6H_4Me-4).[10] Relevant to the results described herein are compounds in which the hydrido-ligand is the only bridging group. Hayter [5] observed the formation of the mixed-metal species $[MM'(\mu\text{-}H)(CO)_{10}]^-$ (M = Cr, M′ = Mo or W; M = Mo, M′ = W), although salts of these anions were not isolated in the pure state. Recently, however, an efficient synthesis of the salts $[NEt_4][CrM(\mu\text{-}H)(CO)_{10}]$ (M = Mo or W) has been reported by Darensbourg and Deaton,[11] allowing complete characterisation. Also known are the series of compounds $[MM'(\mu\text{-}H)(CO)_{10}]$ (M = Cr, Mo, or W; M′ = Mn or Re), which were the first well defined complexes to be reported [12] in which transition elements from different periodic groups are linked by a hydrogen atom. Other heteronuclear dimetal compounds in which the two metal atoms are linked only by a hydrido-ligand are the iron–niobium and –tantalum complexes $[FeM(\mu\text{-}H)(CO)_5(\eta\text{-}C_5H_5)_2]$ (M = Nb or Ta),[13] and the compounds $[MTa(\mu\text{-}H)(CO)_6(\eta\text{-}C_5H_5)_2]$ (M = Cr, Mo, or W) and $[MnTa(\mu\text{-}H)(CO)_3(\eta\text{-}C_5H_5)_3]$.[14]



	M	M′	R	L
(1)	Cr	Au	Ph	CO
(2)	Mo	Au	Ph	CO
(3)	W	Au	Ph	CO
(4)	W	Au	Ph	$P(OMe)_3$
(5)	Cr	Ag	Me	CO
(6)	W	Ag	Me	CO
(7)	W	Ag	Me	$P(OMe)_3$

Our interest in preparing and studying the compounds (1)—(7) was stimulated by an appreciation that the groups $M(CO)_5$ (M = Cr, Mo, or W) and $M'(PR_3)^+$ (M′ = Au, R = Ph; M′ = Ag, R = Me) are isolobal.[15,16] These fragments possess one vacant frontier orbital, and are able to accept an electron pair from a suitable donor ligand. Since the anions $[MH(CO)_5]^-$ have a known [11,17,18] propensity to combine with $M(CO)_5$ fragments to give the species $[M_2(\mu\text{-}H)(CO)_{10}]^-$, it followed that a similar reaction might occur between $[MH(CO)_5]^-$ and $M'(PR_3)^+$ to afford neutral complexes containing M(μ-H)M′ linkages.

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* 2,2,2,2,2-Pentacarbonyl-μ-hydrido-1-triphenylphosphinegold-chromium(*Au–Cr*).

Supplementary data available (No. SUP 56001, 25 pp.): structure factors, H-atom co-ordinates, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1983, Issue 1, pp. xvii—xix.

Table 1. Analytical [a] and physical data for the bimetallic hydrido-bridged complexes

Compound [b]	M.p. $(\theta_c/^\circ C)$ (decomp.)	$\nu_{max.}(CO)$ [c]/cm^{-1}	Analysis (%)	
			C	H
(1) $[AuCr(\mu\text{-}H)(CO)_5(PPh_3)]$	115—119	2 058m, 1 979w, 1 934vs (br)	42.1 (42.3)	2.4 (2.5)
(2) $[AuMo(\mu\text{-}H)(CO)_5(PPh_3)]$	108—112	2 069m, 1 986w, 1 942vs (br)	39.4 (39.7)	2.2 (2.3)
(3) $[AuW(\mu\text{-}H)(CO)_5(PPh_3)]$	104—107	2 067m, 1 978w, 1 934vs (br)	35.5 (35.2)	1.9 (2.0)
(4) $[AuW(\mu\text{-}H)(CO)_4\{P(OMe)_3\}(PPh_3)]$	88—92	2 020m, 1 901vs (br)	34.4 (34.1)	3.0 (2.8)
(5) $[AgCr(\mu\text{-}H)(CO)_5(PMe_3)]$	120—123	2 052m, 1 970w, 1 926vs (br)	25.9 (25.5)	2.9 (2.7)
(6) $[AgW(\mu\text{-}H)(CO)_5(PMe_3)]$	107—109	2 063m, 1 970w, 1 926vs (br)	19.0 (18.9)	2.0 (2.0)
(7) $[AgW(\mu\text{-}H)(CO)_4\{P(OMe)_3\}(PMe_3)]$	90—94	2 013m, 1 891vs (br)	20.2 (19.8)	3.5 (3.1)

[a] Calculated values are given in parentheses. [b] All compounds are yellow. [c] Measured in dichloromethane.

Table 2. Hydrogen-1, carbon-13, and phosphorus-31 n.m.r. data [a] for the bimetal compounds

Compound	^{1}H [b]	$^{13}C\text{-}\{^{1}H\}$ [c]	$^{31}P\text{-}\{^{1}H\}$ [d]
(1) [e]	−5.96 (s, 1 H, μ-H), 7.51—7.56 (m, 15 H, Ph)	224.3 (1 CO), 219.6 (4 CO), 134.4 [d, C^2(Ph), J(PC) 14], 132.1 [C^4(Ph)], 129.6 [d, C^3(Ph), J(PC) 10], 129.5 [d, C^1 (Ph), J(PC) 56]	49.8 (s)
(2) [f]	−2.42 (s, 1 H, μ-H), 7.45—7.57 (m, 15 H, Ph)	213.1 (1 CO), 208.3 (4 CO), 134.3 [d, C^2(Ph), J(PC) 14], 132.0 [C^4(Ph)], 129.6 [d, C^1(Ph), J(PC) 53], 129.5 [d, C^3(Ph), J(PC) 12] [g]	50.4 (s) [h]
(3) [i]	−2.69 [s, 1 H, μ-H, J(WH) 46], 7.45—7.61 (m, 15 H, Ph)	201.2 (1 CO), 198.9 [4 CO, J(WC) 123], 134.5 [d, C^2(Ph), J(PC) 14], 132.1 [C^4(Ph)], 130.7 [s (half of d), C^1(Ph)], 128.7 [d, C^3(Ph), J(PC) 12]	52.9 (s)
(4) [j]	−2.65 [d of d, 1 H, μ-H, J(PH) 108 and 19, J(WH) 44], 3.59 [d, 9 H, OMe, J(PH) 12], 7.45—7.61 (m, 15 H, Ph)	206.7 [d, 1 CO, J(PC) 38], 205.2 [d, 1 CO, J(PC) 11], 201.6 [d, 2 CO, J(PC) 11, J(WC) 126] 134.2 [d, C^2(Ph), J(PC) 14], 131.5 [C^4(Ph)], 130.3 [d, C^1(Ph), J(PC) 51], 129.2 [d, C^3(Ph), J(PC) 11], 51.9 (OMe) [h]	155.9 [d, $P(OMe)_3$, J(PP) 16, J(WP) 360], 52.1 [d, PPh_3, J(PP) 16] [k]
(5) [l]	−7.11 (s, 1 H, μ-H), 1.52 [d, 9 H, Me, J(PH) 6]	224.8 (1 CO), 219.7 (4 CO), 15.2 [d, Me, J(PC) 20]	−36.7 (s) [h]
(6) [m]	−3.48 [s, 1 H, μ-H, J(WH) 42], 1.49 [d, 9 H, Me, J(PH) 7]	200.4 (1 CO), 197.9 [4 CO, J(WH) 120], 15.3 [d, Me, J(PC) 22]	−32.3 (s) [h]
(7) [n]	−4.63 [d, 1 H, μ-H, J(PH) 22, J(WH) 43], 1.38 [d, 9 H, Me, J(PH) 7], 3.59 [d, 9 H, OMe, J(PH) 12]	204.9 [d, 1 CO, J(PC) 39], 203.2 [d, 1 CO, J(PC) 9], 200.9 [d, 2 CO, J(PC) 11, J(WC) 121], 52.0 (OMe), 15.2 [d, Me, J(PC) 15] [h]	146.7 [s, $P(OMe)_3$, J(WP) 358], −37.1 (s, PMe_3)

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz. [b] Measured in CD_2Cl_2 at room temperature, unless otherwise stated. [c] Measured in CD_2Cl_2–CH_2Cl_2 at room temperature unless otherwise stated, positive values of δ representing shifts to high frequency of $SiMe_4$. [d] Measured in CD_2Cl_2 at room temperature unless otherwise stated, δ values being positive to high frequency of 85% H_3PO_4 (external). [e] At −90 °C, the μ-H resonance (δ −5.86) was a doublet [J(PH) 105 Hz], and, corresponding to this observation, at −50 °C (in $CDCl_3$) the selectively ^{1}H-decoupled ^{31}P signal (δ 49.2) was also a doublet. [f] At −90 °C, ^{1}H, δ −2.37 [d, 1 H, μ-H, J(PH) 117 Hz]. [g] Measured at −50 °C. [h] Measured in $CDCl_3$. [i] Low-temperature data (−90 °C): ^{1}H, δ −2.48 [d, 1H, μ-H, J(PH) 107, J(WH) 44]; $^{31}P\text{-}\{^{1}H\}$, δ 49.0 (s); $^{13}C\text{-}\{^{1}H\}$, δ 202.1 (1 CO) and 199.1 [4 CO, J(WC) 125 Hz]. [j] Low-temperature data (−90 °C): ^{1}H, δ −2.67 [d, of d, 1 H, μ-H, J(PH) 106 and 20, J(WH) 45]; $^{13}C\text{-}\{^{1}H\}$, δ 207.9 [d, 1 CO, J(PC) 37], 205.7 [s(br), 1 CO], and 201.2 [s (br), 2 CO, J(WC) 124 Hz]. [k] Measured at −90 °C. [l] At −90 °C, ^{1}H, δ −7.06 [s(br), 1 H, μ-H]. [m] At −90 °C, ^{1}H, δ *ca.* −3.4 (vbr, 1 H, μ-H). [n] At −90 °C, ^{1}H, δ *ca.* −4.4 (vbr, 1 H, μ-H).

Results and Discussion

Treatment of tetrahydrofuran (thf) solutions of the salts $[N(PPh_3)_2][MH(CO)_4L]$ [M = Cr or W, L = CO; M = W, L = $P(OMe)_3$] [17–19] with $[AuCl(PPh_3)]$, in the presence of $TlPF_6$ to remove chloride anions,[20] affords the yellow crystalline compounds (1), (3), and (4) in *ca.* 60—75% yield. The anion $[MoH(CO)_5]^-$ is reported [17] to be unstable in solution above 0 °C, and so the gold–molybdenum compound (2) was prepared from the reaction between $[N(PPh_3)_2][Mo_2(\mu\text{-}H)(CO)_{10}]$ [21] and $[AuCl(PPh_3)]$ in dichloromethane, using $TlPF_6$. This reaction corresponds formally to the displacement of an $Mo(CO)_5$ fragment from $[Mo_2(\mu\text{-}H)(CO)_{10}]^-$ by the isolobal $Au(PPh_3)^+$ group. Compounds (1) and (3) can be similarly synthesised from their respective salts $[N(PPh_3)_2][M_2(\mu\text{-}H)(CO)_{10}]$ (M = Cr or W), but in lower yield than when the anions $[MH(CO)_5]^-$ are employed. The hexacarbonyls of Cr, Mo, or W are by-products of the preparation of compounds (1)—(3) using the dimetal monoanions $[M_2(\mu\text{-}H)(CO)_{10}]^-$ as precursors. Surprisingly, complex (3) can also be obtained (*ca.* 30%) by treating a diethyl ether solution of $[W_2(\mu\text{-}H)(CO)_9(NO)]$ with $[AuMe(PPh_3)]$ at room temperature. The mechanism of this reaction is unknown, but based on previous work [22] a compound of formulation $[AuW_2(CO)_9(NO)(PPh_3)]$ might have been anticipated as the product.

Compounds (1)—(4) were characterised by microanalysis, and by their i.r. and n.m.r. properties (Tables 1 and 2). The spectroscopic data for compounds (1)—(3) are very similar, implying similar structures. The ^{1}H n.m.r. spectra show a characteristic high-field resonance for the μ-H ligand, which, although a singlet at room temperature, appears as a doublet when the spectrum is measured at −90 °C, owing to ^{31}P–^{1}H coupling. The J(PH) values [compound (1) 105, (2) 117, and (3) 107 Hz] are as expected for a *transoid* Ph_3P–Au–H arrangement. In the ^{1}H n.m.r. spectrum of $[AuIrH_2(\mu\text{-}H)(PPh_3)_4][BF_4]$ the ^{31}P–^{1}H coupling for the unit *trans*-Ph_3P-Au(μ-H)Ir is 79 Hz.[2] In the room-temperature ^{1}H n.m.r. spectrum of compound (4) the hydrido-ligand signal appears as a doublet of doublets. The larger J(PH) value (108 Hz) is

Table 3. Bond lengths (Å) and interbond angles (°) for [AuCr(μ-H)(CO)$_5$(PPh$_3$)] (1), with estimated standard deviations in parentheses

Au–Cr	2.770(2)	Au–H	1.72(11)	C(6)–C(11)	1.399(12)	C(7)–C(8)	1.408(16)
Au–P	2.290(3)	Cr–H	1.64(12)	C(8)–C(9)	1.369(14)	C(9)–C(10)	1.386(15)
Cr–C(1)	1.860(12)	Cr–C(2)	1.899(7)	C(10)–C(11)	1.395(14)	C(12)–C(13)	1.381(15)
Cr–C(3)	1.914(12)	Cr–C(4)	1.872(12)	C(12)–C(17)	1.392(16)	C(13)–C(14)	1.381(16)
Cr–C(5)	1.912(7)	P–C(11)	1.806(10)	C(14)–C(15)	1.385(18)	C(15)–C(16)	1.363(15)
P–C(17)	1.811(9)	P–C(23)	1.805(7)	C(16)–C(17)	1.413(14)	C(18)–C(19)	1.390(10)
C(1)–O(1)	1.140(16)	C(2)–O(2)	1.147(10)	C(18)–C(23)	1.398(14)	C(19)–C(20)	1.386(16)
C(3)–O(3)	1.135(15)	C(4)–O(4)	1.151(16)	C(20)–C(21)	1.389(15)	C(21)–C(22)	1.383(10)
C(5)–O(5)	1.148(9)	C(6)–C(7)	1.375(15)	C(22)–C(23)	1.400(14)		

Cr–Au–H	34(4)	Cr–Au–P	155.4(1)	C(17)–P–C(23)	105.5(4)	Cr–C(1)–O(1)	176.3(9)
H–Au–P	170(4)	Au–Cr–H	36(4)	Cr–C(2)–O(2)	173.7(11)	Cr–C(3)–O(3)	179.1(8)
Au–Cr–C(1)	161.2(2)	H–Cr–C(1)	163(4)	Cr–C(4)–O(4)	177.7(11)	Cr–C(5)–O(5)	174.9(11)
Au–Cr–C(2)	111.7(4)	H–Cr–C(2)	80(3)	C(7)–C(6)–C(11)	120.8(9)	C(6)–C(7)–C(8)	119.6(9)
C(1)–Cr–C(2)	85.0(4)	Au–Cr–C(3)	76.6(4)	C(7)–C(8)–C(9)	119.8(10)	C(8)–C(9)–C(10)	120.7(10)
H–Cr–C(3)	92(4)	C(1)–Cr–C(3)	95.5(5)	C(9)–C(10)–C(11)	120.2(9)	P–C(11)–C(6)	119.8(7)
C(2)–Cr–C(3)	89.7(4)	Au–Cr–C(4)	97.4(4)	P–C(11)–C(10)	121.3(7)	C(6)–C(11)–C(10)	118.9(9)
H–Cr–C(4)	83(4)	C(1)–Cr–C(4)	90.2(5)	C(13)–C(12)–C(17)	119.6(10)	C(12)–C(13)–C(14)	120.9(12)
C(2)–Cr–C(4)	92.3(4)	C(3)–Cr–C(4)	174.0(6)	C(13)–C(14)–C(15)	119.0(10)	C(14)–C(15)–C(16)	121.8(11)
Au–Cr–C(5)	74.1(4)	H–Cr–C(5)	107(3)	C(15)–C(16)–C(17)	118.9(11)	P–C(17)–C(12)	123.3(7)
C(1)–Cr–C(5)	88.7(4)	C(2)–Cr–C(5)	173.0(5)	P–C(17)–C(16)	116.9(8)	C(12)–C(17)–C(16)	119.7(9)
C(3)–Cr–C(5)	88.0(4)	C(4)–Cr–C(5)	90.7(4)	C(19)–C(18)–C(23)	120.1(9)	C(18)–C(19)–C(20)	121.0(10)
Au–H–Cr	111(5)	Au–P–C(11)	113.7(3)	C(19)–C(20)–C(21)	119.1(7)	C(20)–C(21)–C(22)	120.4(10)
Au–P–C(17)	111.6(3)	C(11)–P–C(17)	107.2(5)	C(21)–C(22)–C(23)	120.9(10)	P–C(23)–C(18)	123.2(7)
Au–P–C(23)	112.5(4)	C(11)–P–C(23)	105.9(4)	P–C(23)–C(22)	118.3(7)	C(18)–C(23)–C(22)	118.5(7)

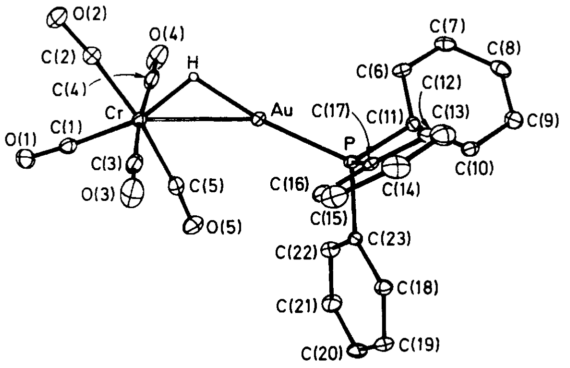

Figure 1. Molecular geometry of [AuCr(μ-H)(CO)$_5$(PPh$_3$)] (1). Atomic thermal ellipsoids are drawn to enclose 30% probability density, with the hydrogen atom as a sphere of arbitrary radius; phenyl-group hydrogen atoms are omitted for clarity

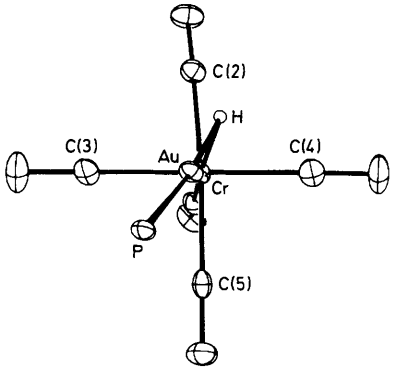

Figure 2. Compound (1) viewed nearly parallel to the Au–Cr vector showing the orientation of Au–(μ-H)–Cr and Cr(CO)$_5$ moieties, drawn as for Figure 1 with phenyl groups omitted entirely

assigned to the *transoid* Ph$_3$P–Au–H fragment, and the smaller coupling (19 Hz) to the (MeO)$_3$P–W–H moiety. Tungsten (^{183}W) satellite peaks are visible on the μ-H ligand signal of compound (4), and also on that of (3).

The ^{13}C-{^{1}H} n.m.r. spectra of compounds (1)—(3) at ambient temperatures show two CO ligand signals of relative intensity 1 : 4, in accord with the presence of the M(CO)$_5$ groups. For compound (4) there are three CO resonances (relative intensity 1 : 1 : 2), each a doublet owing to ^{31}P–^{13}C coupling. One of these doublets, corresponding to one CO ligand, shows a significantly larger coupling (38 Hz) than the others (11 Hz), and is assigned to the CO group *trans* to P(OMe)$_3$. The latter group in the precursor [N(PPh$_3$)$_2$][WH(CO)$_4${P(OMe)$_3$}] has a *cis* orientation relative to the hydrido-ligand,[19] and the ^{13}C-{^{1}H} n.m.r. spectra of the anion show three CO signals which are doublets with *J*(PC) 42, 11, and 7 Hz, respectively. Since these values are similar to those found for compound (4) we assign the latter a structure with an equatorial CO group substituted by a P(OMe)$_3$ ligand.

To establish in detail the molecular structures of the hydrido-bridged compounds (1)—(3), a single-crystal *X*-ray diffraction study was performed on (1). Further discussion of the n.m.r. data, and some observations on the dynamic properties of these compounds in solution, are deferred until the *X*-ray diffraction results have been presented.

The details of the *X*-ray diffraction study are given in the Experimental section, and bond lengths and interbond angles in Table 3. The molecular geometry is illustrated in Figures 1 and 2, the former showing the atomic labelling scheme. The molecule of compound (1) in the solid state shows C_1 symmetry, and may be considered to consist of Cr(CO)$_5$ and Au(PPh$_3$) moieties bridged by a hydrido-ligand. The Cr(CO)$_5$ moiety shows approximate C_{4v} symmetry, albeit with deviations of up to 5° in C–Cr–C angles. The Au–H–Cr unit is markedly bent, as has been observed for other three-centre two-electron unsupported M–H–M systems in, for example, [M$_2$(μ-H)(CO)$_{10}$]$^-$ (M = Cr, Mo, or W) and [W$_2$(μ-H)(CO)$_8$(NO)L] [L = CO or P(OMe)$_3$].[3,7,21] The metal–metal distance in compound (1) [2.770(2) Å] is much shorter than in related complexes; *e.g.* in [K(crypt-222)][Cr$_2$(μ-H)(CO)$_{10}$] (crypt-

222 = $C_{18}H_{36}N_2O_6$) the Cr–Cr distance is 3.300(4) Å (at 20 K, by neutron diffraction).[7c]

In addition, the Au–H–Cr angle is much smaller [111(5)°], although of necessity it is poorly defined by *X*-ray diffraction {*cf.* in [K(crypt-222)][$Cr_2(\mu\text{-}H)(CO)_{10}$], Cr–H–Cr = 145.2(3)° by neutron diffraction and 158.5° by *X*-ray diffraction}. The more bent geometry in compound (1) may indicate a greater degree of direct metal–metal interaction than in the dimeric Group 6 monoanions. The non-hydrogen skeleton of the molecule reflects the geometry of the Au–H–Cr bridge, and the stereoelectronic requirements of the μ-H ligand. Thus the P–Au–Cr and C(1)–Cr–Au moieties are non-linear [angles 155.4(1) and 161.2(2)°, respectively] and the Au–Cr–$C_{eq.}$ angles fall into two groups: acute [for C(3), 76.6(4) and C(5), 74.1(4)°] and obtuse [for C(2), 111.7(4) and C(4), 97.4(4)°]. These angular distortions are a consequence of the Au–μ-H system being staggered with respect to the equatorial carbonyl ligands, as shown in Figure 2. Similar staggering of the M–μ-H moiety has been noted for all the Group 6 dimetal species discussed above.[3,7,21] The P–Au–Cr–$C_{eq.}$ torsion angles show this orientational preference clearly; the angles are 141.8(3), 57.6(3), −122.8(3), and −34.2(3)° for C(2), C(3), C(4), and C(5), respectively. That the μ-H ligand lies *transoid* to the phosphine and axial CO ligands is indicated both by the P–Au–H and C(1)–Cr–H angles [170(4) and 163(4)°, respectively] and by the P–Au–Cr–C(1) torsion angle [−9.5(3)°]. The Cr–μ-H distance [1.64(12) Å] is reasonable in view of other such bond lengths, *e.g.* in [K(crypt-222)][$Cr_2(\mu\text{-}H)(CO)_{10}$], Cr–H = 1.60 and 1.77 Å by *X*-ray and 1.723(5) and 1.734(5) Å by neutron diffraction.[7c] The recently studied [18] anion [$H_2B(\mu\text{-}H)_2Cr(CO)_4$]$^-$ shows somewhat longer Cr–μ-H distances, 1.88(7) Å determined by *X*-ray diffraction. The Au–μ-H distance [1.72(11) Å] in compound (1) would appear reasonable in the light of more precisely determined Os–μ-H and Ir–μ-H distances.[3]

Other features of the molecular geometry of compound (1) are unremarkable. Thus the Au–P distance is of the usual dimensions [2.290(3) Å].[22] The Cr–CO linkages are near linear [varying between 173.7(11) and 179.1(8)°], and show only a very small *trans* effect [Cr–C(1), 1.860(12), mean Cr–$C_{eq.}$ = 1.899(12) Å]. The anion [$CrH(CO)_5$]$^-$ shows a similarly feeble *trans* effect of a terminal hydrido-ligand.[18]

The solid-state structures of the anions [$M_2(\mu\text{-}H)(CO)_{10}$]$^-$ have been shown to be strongly dependent on intermolecular forces, in particular the nature of the cation.[3] Although we have no direct evidence for comparable flexibility in the solid-state conformation of (1), the n.m.r. studies described below are consistent with the complex in solution undergoing a low-energy rearrangement involving effective rotation of the Ph_3P–Au–μ-H moiety about the C_4 axis of the $Cr(CO)_5$ group.

Having established the molecular structure of compound (1), it can be seen how the isolobal relationships $Cr(CO)_5 \xleftrightarrow[o]{} W(CO)_5 \xleftrightarrow[o]{} Re(CO)_5{}^+ \xleftrightarrow[o]{} Au(PPh_3)^+$ account for the existence of the four compounds [NEt_4][$CrM(\mu\text{-}H)(CO)_{10}$] (M = Cr or W),[11] [$CrRe(\mu\text{-}H)(CO)_{10}$],[12] and [$AuCr(\mu\text{-}H)(CO)_5(PPh_3)$] (1). Moreover, since the groups $Au(PPh_3)^+$ and $Ag(PMe_3)^+$ are isolobal the compounds [$AgM(\mu\text{-}H)(CO)_5(PMe_3)$] should exist. Compounds (5)—(7) were thus prepared by treating thf solutions of the salts [$N(PPh_3)_2$][$MH(CO)_4L$] [M = Cr or W, L = CO; M = W, L = $P(OMe)_3$] with [$AgI(PMe_3)$], in the presence of $TlPF_6$. The silver–chromium and -tungsten compounds (Table 1) were obtained in *ca.* 60% yield. Unfortunately, reactions of the anions [$M_2(\mu\text{-}H)(CO)_{10}$]$^-$ (M = Cr, Mo, or W) with [$AgI(PMe_3)$] in either thf or CH_2Cl_2 solution afforded inseparable mixtures, and hence the silver–molybdenum analogue of compound (2) could not be prepared in this way. The i.r. and n.m.r. spectra for compounds (5)—(7) (Tables 1 and 2) are similar to those observed for (1)—(4), implying similar structures.

The n.m.r. data for complexes (1)—(7) vary with temperature, indicating dynamic behaviour in solution. As mentioned above, the strong ^{31}P–^1H coupling observed for the μ-H ligand signal in the ^1H n.m.r. spectra of (1)—(3), measured at −90 °C in CD_2Cl_2, is absent at ambient temperatures. In contrast, this coupling (108 Hz) is present in the room-temperature spectrum of compound (4) (Table 2) in the same solvent, although on warming this peak becomes very broad at 40 °C. When the ^1H n.m.r. spectrum of (2) is measured in [$^2H_8$]toluene no ^{31}P–^1H coupling between μ-^1H and $^{31}PPh_3$ is observed at ambient temperatures, but on cooling to −90 °C a doublet of doublets is seen. Hence the variation in the ^1H n.m.r. spectra of compounds (1)—(4) with temperature appears to be similar, but the activation energy for the process occurring in CD_2Cl_2 is higher for (4) than for (1)—(3). Moreover, the dynamic behaviour is solvent dependent, as discussed further below.

The ^{31}P-{^1H} n.m.r. spectra of compounds (1)—(3) show sharp singlets at room temperature, and these peaks are not broadened as the samples are cooled to −90 °C, although there is an appreciable change in the chemical shifts (Table 2). For (4), the ^{31}P-{^1H} n.m.r. spectrum, measured in CD_2Cl_2, does not significantly change between 35 and −90 °C, except for a sharpening of the two peaks on cooling, allowing the ^{31}P–^{31}P coupling (16 Hz) to be resolved. Measurement of the ^{31}P-{^1H} n.m.r. spectrum of (4) in [$^2H_8$]toluene reveals two sharp singlets down to *ca.* −60 °C, which become appreciably broad at −75 °C. At −90 °C the two resonances are sharp doublets [*J*(PP) 16 Hz].

From the ^1H and ^{31}P-{^1H} n.m.r. data we conclude that an exchange process is occurring between PPh_3 groups. Dynamic processes involving the hydrido-ligands are ruled out by the observation of ^{183}W satellite peaks on the μ-H signal in the ^1H n.m.r. spectra of compounds (3) and (4) and by the ^{31}P–^1H coupling between μ-H and $P(OMe)_3$ in (4). Furthermore, only a process involving PPh_3 exchange can account for the variable-temperature ^{31}P-{^1H} n.m.r. results obtained for (4) in [$^2H_8$]toluene. Addition of free PPh_3 to ^{31}P-{^1H} n.m.r. samples of compounds (1)—(3) results in a single sharp resonance with chemical shift intermediate between that of the respective dimetal species and free PPh_3. Moreover, when the same experiment is performed with (4), the peaks for $Au(PPh_3)$ and PPh_3 merge, but the resonance due to the $P(OMe)_3$ ligand is unaffected. It is thus evident that the complexes in solution readily exchange PPh_3 groups for free PPh_3. If the pure complexes themselves dissociate, the amount of uncomplexed PPh_3 in solution must be small otherwise broadening of the resonances for compounds (1)—(3) would be expected near the coalescence temperature.

The solvent and ligand dependence of the fluxional process which causes loss of ^{31}P–^1H coupling between the μ-H and PPh_3 ligands in the ^1H spectra of compounds (1)—(4) is interesting. For (1)—(3) in CD_2Cl_2 the coalescence temperature for the μ-H peaks is −58 ± 5 °C corresponding to a $\Delta G^{\ddagger}(T_c)$ value of 42 ± 1 kJ mol^{-1}. For (4), in the same solvent, T_c is 38 ± 5 °C and $\Delta G^{\ddagger}(T_c)$ is 62 ± 1 kJ mol^{-1}, while for this complex in [$^2H_8$]toluene, T_c = −70 ± 5 °C, corresponding to a $\Delta G^{\ddagger}(T_c)$ value of 40 ± 1 kJ mol^{-1}. Furthermore, for (1), measured in $CDCl_3$, T_c = 18 ± 5 °C leading to $\Delta G^{\ddagger}(T_c)$ = 58 ± 1 kJ mol^{-1}. Again changing the solvent has a large effect on the free energy of the process.

The carbonyl ligands in compounds (1)—(3) are also undergoing site exchange. At ambient temperatures, in the ^{13}C-{^1H} n.m.r. spectra the equatorial CO ligands give rise to only one resonance, and even at −90 °C only a singlet peak is observed for these ligands in the spectrum of (3). The basic pattern of

^{13}C-{^1H} n.m.r. CO signals for (4) is the same at −90 °C as at room temperature although obviously two equatorial carbonyl-group environments are visible. In compounds (1)—(3), rotation of the $M(CO)_5$ (M = Cr, Mo, or W) fragments about the Au−M vector is a possible mechanism to account for the ^{13}C-{^1H} n.m.r. data. It is not clear whether the equivalence of the two mutually *trans* equatorial CO ligands in (4) is due to a dynamic process or to the symmetry of the molecule itself.

Examination of the ^1H and ^{31}P-{^1H} n.m.r. spectra of compounds (5)—(7) shows that these complexes are not only undergoing an exchange of PMe_3 groups between molecules, but also that the $MH(CO)_4L$ [L = CO or $P(OMe)_3$] groups are labile at room temperature. Thus the high-field ^1H n.m.r. signals for the μ-H groups show no coupling with the ^{31}P nuclei of the PMe_3 ligands or with the silver nuclei (^{107}Ag or ^{109}Ag). At −90 °C these peaks become very broad. Moreover, in the ^{31}P-{^1H} n.m.r. spectra of compounds (5)—(7) there is no ^{31}P–^{107}Ag(^{109}Ag) coupling. Lability of PR_3 groups bonded to silver has been previously observed.[23] In the context of the dynamic behaviour of compounds (5)—(7), it is interesting that Hayter[5] observed that mixtures of the anions $[M_2(\mu\text{-}H)(CO)_{10}]^-$ and $[M'_2(\mu\text{-}H)(CO)_{10}]^-$ undergo scrambling reactions in thf at 80 °C to afford statistical quantities of the appropriate mixed-metal anions $[MM'(\mu\text{-}H)(CO)_{10}]^-$. These reactions obviously involve scrambling of $[MH(CO)_5]^-$ fragments between molecules.

As was observed for compounds (1)—(4), the ^{13}C-{^1H} n.m.r. spectra of (5) and (6), measured at room temperature, display only one equatorial CO ligand environment, while the spectrum of (7) shows that the two mutually *trans* equatorial carbonyl groups are equivalent. At −90 °C the CO resonances for the three compounds are broadened. The dynamic process discussed above, involving dissociation of $MH(CO)_4L$ fragments, would provide a mechanism for the site exchange of the equatorial CO groups, as would a mechanism of $M(CO)_4L$ group rotation similar to that proposed for (1)—(4). Precise conclusions from the data are, therefore, not possible.

The compounds (1)—(7) in toluene at 80 °C do not react with $[AuMe(PPh_3)]$ to afford trimetal species, *e.g.* $[Au_2Cr(CO)_5(PPh_3)_2]$ or $[AgAuW(CO)_5(PMe_3)(PPh_3)]$, although complexes of this kind may well be capable of existence.[16]

Experimental

All reactions were carried out under an oxygen-free nitrogen atmosphere, using Schlenk-tube techniques. Light petroleum refers to that fraction of b.p. 40—60 °C. The instrumentation employed has been described elsewhere.[22b] Established methods were used to prepare the compounds $[N(PPh_3)_2][MH(CO)_4L]$ [M = Cr or W, L = CO; M = W, L = $P(OMe)_3$],[17,19] $[W_2(\mu\text{-}H)(CO)_9(NO)]$,[24] $[AuX(PPh_3)]$ (X = Cl[25] or Me[26]), and $[AgI(PMe_3)]$.[27] The complexes $[N(PPh_3)_2][M_2(\mu\text{-}H)(CO)_{10}]$ (M = Cr, Mo, or W) were synthesised by adaptation of published routes.[5,21] Analytical and other data for the new compounds are given in Table 1. Table 2 summarises the results of n.m.r. measurements. Alumina used for chromatography columns (*ca.* 15 × 3 cm) was B.D.H. Brockman Activity II.

Reactions between the Salts $[N(PPh_3)_2][MH(CO)_4L]$ [M = Cr *or* W, L = CO; M = W, L = $P(OMe)_3$] *and* $[AuCl(PPh_3)]$.—A thf (50 cm³) solution of $[N(PPh_3)_2][CrH(CO)_5]$ (0.50 g, 0.68 mmol) was treated with $[AuCl(PPh_3)]$ (0.34 g, 0.69 mmol) in $TlPF_6$ (0.50 g, 1.43 mmol), and the mixture was stirred at room temperature for 15 min. After filtration of the mixture through a Celite pad (*ca.* 1 × 3 cm), solvent was removed *in vacuo* and the crude residue was dissolved in dichloromethane–light petroleum (1 : 4) and chromatographed. Elution with the same solvent mixture afforded one yellow band containing the product. After removal of solvent *in vacuo*, the residue was crystallised from dichloromethane–light petroleum to give yellow *crystals* of $[AuCr(\mu\text{-}H)(CO)_5(PPh_3)]$ (1) (0.34 g, 76%).

Yellow *crystals* of $[AuW(\mu\text{-}H)(CO)_5(PPh_3)]$ (3) (0.32 g, 70%) were similarly prepared from $[N(PPh_3)_2][WH(CO)_5]$ (0.50 g, 0.58 mmol), $[AuCl(PPh_3)]$ (0.29 g, 0.59 mmol), and $TlPF_6$ (0.50 g, 1.43 mmol). Using the same procedures, the compound $[AuW(\mu\text{-}H)(CO)_4\{P(OMe)_3\}(PPh_3)]$ (4) (0.29 g, 63%) was obtained as *crystals* from $[N(PPh_3)_2][WH(CO)_4\{P(OMe)_3\}]$ (0.50 g, 0.52 mmol), $[AuCl(PPh_3)]$ (0.26 g, 0.53 mmol), and $TlPF_6$ (0.50 g, 1.43 mmol).

Reactions between the Salts $[N(PPh_3)_2][M_2(\mu\text{-}H)(CO)_{10}]$ (M = Cr, Mo, *or* W) *and* $[AuCl(PPh_3)]$.—A dichloromethane (50 cm³) solution of $[N(PPh_3)_2][Mo_2(\mu\text{-}H)(CO)_{10}]$ (0.41 g, 0.41 mmol) was treated with $[AuCl(PPh_3)]$ (0.20 g, 0.40 mmol) and $TlPF_6$ (0.40 g, 1.15 mmol), and the mixture was stirred at room temperature for 1 h. After filtration of the yellow mixture through a Celite pad (*ca.* 1 × 3 cm), solvent was removed *in vacuo* and the residue dissolved in dichloromethane–light petroleum (1 : 4). Chromatography, eluting with the same solvent mixture, afforded a yellow solution. Removal of solvent under reduced pressure gave a residue which was crystallised from dichloromethane–light petroleum to yield yellow *crystals* of $[AuMo(\mu\text{-}H)(CO)_5(PPh_3)]$ (2) (0.11 g, 39%).

The complexes $[AuCr(\mu\text{-}H)(CO)_5(PPh_3)]$ (1) (0.09 g, 42%) and $[AuW(\mu\text{-}H)(CO)_5(PPh_3)]$ (3) (0.06 g, 19%) were similarly prepared from $[N(PPh_3)_2][M_2(\mu\text{-}H)(CO)_{10}]$ [M = Cr (0.30 g, 0.33 mmol) or W (0.48 g, 0.40 mmol)], $[AuCl(PPh_3)]$ [for (1) 0.16 g, 0.32 mmol; for (3) 0.20 g, 0.40 mmol], and $TlPF_6$ (0.40 g, 1.15 mmol). Samples of (1) and (3) synthesised in this manner had identical i.r. and ^{31}P-{^1H} n.m.r. spectra to those of the same products prepared from $[N(PPh_3)_2][MH(CO)_5]$ (M = Cr or W).

Reaction between the Compounds $[W_2(\mu\text{-}H)(CO)_9(NO)]$ *and* $[AuMe(PPh_3)]$.—A diethyl ether (30 cm³) solution of $[W_2(\mu\text{-}H)(CO)_9(NO)]$ (0.21 g, 0.32 mmol) was treated with $[AuMe(PPh_3)]$ (0.15 g, 0.32 mmol) and the mixture was stirred at room temperature overnight. After removal of the solvent under reduced pressure, the residue was dissolved in dichloromethane–light petroleum (1 : 4) and chromatographed. Elution with the same solvent mixture led to the isolation of compound (3) (0.08 g, 32%) (identified by i.r. and ^{31}P-{^1H} n.m.r. spectroscopy), after removal of solvent *in vacuo* and recrystallisation from dichloromethane–light petroleum.

Reactions between the Salts $[N(PPh_3)_2][MH(CO)_4L]$ [M = Cr *or* W, L = CO; M = W, L = $P(OMe)_3$] *and* $[AgI(PMe_3)]$.—A thf (50 cm³) solution of $[N(PPh_3)_2][CrH(CO)_5]$ (0.60 g, 0.82 mmol) was treated with $[AgI(PMe_3)]$ (0.26 g, 0.84 mmol) and $TlPF_6$ (0.60 g, 1.72 mmol), and the mixture was stirred for 15 min. After filtration through a Celite pad (*ca.* 1 × 3 cm), solvent was removed *in vacuo* and the residue extracted with diethyl ether (4 × 20 cm³). The extracts were again filtered, and the volume reduced to *ca.* 5 cm³. Addition of light petroleum (*ca.* 30 cm³), followed by cooling to *ca.* −20 °C, afforded pale yellow *microcrystals* of $[AgCr(\mu\text{-}H)(CO)_5(PMe_3)]$ (5) (0.20 g, 65%).

In a similar manner, yellow *microcrystals* of $[AgW(\mu\text{-}H)(CO)_5(PMe_3)]$ (6) (0.28 g, 59%) were obtained from $[N(PPh_3)_2][WH(CO)_5]$ (0.80 g, 0.93 mmol), $[AgI(PMe_3)]$ (0.29 g, 0.93 mmol), and $TlPF_6$ (0.70 g, 2.01 mmol). Also, the reaction

Table 4. Atomic positional parameters (fractional co-ordinates) (× 10^4), for complex (1) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*z*	*z*
Au	1 019(1)	4 765(1)	2 126(1)	C(9)	2 800(11)	9 193(9)	858(9)
Cr	1 414(2)	2 922(1)	2 840(1)	C(10)	2 110(10)	8 703(8)	1 652(8)
P	934(2)	6 748(2)	2 462(2)	C(11)	1 824(9)	7 413(7)	1 441(7)
C(1)	1 912(11)	2 159(9)	3 842(8)	C(12)	−1 768(11)	6 955(9)	1 363(8)
O(1)	2 231(10)	1 645(7)	4 402(7)	C(13)	−3 350(11)	6 762(10)	1 192(9)
C(2)	−66(11)	1 171(9)	1 688(9)	C(14)	−4 263(11)	6 269(10)	1 885(9)
O(2)	−927(9)	82(7)	1 078(7)	C(15)	−3 581(11)	5 937(10)	2 738(9)
C(3)	−256(12)	3 244(9)	3 554(9)	C(16)	−2 036(11)	6 080(8)	2 910(8)
O(3)	−1 232(10)	3 454(8)	3 987(9)	C(17)	−1 096(10)	6 615(7)	2 221(7)
C(4)	3 041(12)	2 724(9)	2 067(10)	C(18)	1 367(11)	8 908(8)	4 782(8)
O(4)	4 063(10)	2 596(7)	1 624(9)	C(19)	2 226(1))	9 861(9)	6 021(8)
C(5)	2 881(11)	4 616(9)	4 159(9)	C(20)	3 677(11)	9 943(9)	6 581(8)
O(5)	3 777(8)	5 585(6)	5 004(7)	C(21)	4 288(11)	9 073(9)	5 875(9)
C(6)	2 237(10)	6 629(8)	416(8)	C(22)	3 441(10)	8 118(9)	4 643(8)
C(7)	2 950(11)	7 125(9)	−355(8)	C(23)	1 965(10)	8 016(8)	4 076(7)
C(8)	3 227(11)	8 428(10)	−131(8)	H	824(111)	3 159(93)	1 621(92)

between $[N(PPh_3)_2][WH(CO)_4\{P(OMe)_3\}]$ (0.50 g, 0.52 mmol), $[AgI(PMe_3)]$ (0.16 g, 0.51 mmol), and $TlPF_6$ (0.50 g, 1.43 mmol) gave yellow *microcrystals* of $[AgW(\mu\text{-}H)(CO)_4\{P(OMe)_3\}(PMe_3)]$ (7) (0.19 g, 60%).

Crystal Structure Determination of $[AuCr(\mu\text{-}H)(CO)_5(PPh_3)]$ (1).—Crystals of compound (1) grow from dichloromethane–light petroleum mixtures as yellow prisms. Diffracted intensities were collected for a unique hemisphere of reciprocal space at 210 K from a crystal of dimensions *ca.* 0.47 × 0.24 × 0.33 mm. The latter was mounted under N_2 in a thin-walled glass capillary on a Nicolet *P*3*m* diffractometer operating in the range $4 \leqslant 2\theta \leqslant 50°$. Of a total of 3 684 intensities recorded, 3 429 remained after averaging of duplicated and symmetry-equivalent measurements, and 3 401 of these with $I \geqslant 3\sigma(I)$ were used in structure solution and refinement. A further 400 azimuthal scan data for eight independent reflections were recorded at room temperature, and used in deriving an empirical six-parameter absorption correction. Transmission coefficients for the full data set varied between 0.465 and 0.285.

The structure was solved by conventional heavy-atom methods (Patterson and Fourier) and refined by full-matrix blocked-cascade least squares to give final residual indices * $R = 0.047$, $R' = 0.060$, and $S = 2.16$. A weighting scheme $w = [\sigma^2(F_o) + g|F_o|^2]^{-1}$ ($g = 0.0005$), where $\sigma(F_o)$ is based on counting statistics, was used and gave a satisfactory variation of $w(F_o - |F_c|)^2$ with respect to $|F_o|$, sin θ, $|h|$, $|k|$, and $|l|$. An extinction correction of the form $F_c' = F_c/(1.0 + 0.002xF_c^2/\sin 2\theta)^{\frac{1}{4}}$ was applied, and refined to a value of $x = 6.7(11) \times 10^{-4}$. All phenyl-group hydrogen atoms were located in Fourier difference syntheses and incorporated in the model in an idealised geometry with C–H = 0.96 Å, and isotropic vibrational parameters fixed at *ca.* 1.2 times that of the attached carbon atom. The hydride-hydrogen atom was placed at a position calculated by a potential-energy technique,[28] assigned a fixed isotropic vibrational parameter, and allowed to refine without positional constraints. All other atoms were assigned anisotropic vibrational parameters and allowed to refine without constraint. Final electron-density difference maps showed no features of chemical significance, the largest features being <1 Å from the gold and chromium atoms, all other residual peaks being <1 e Å^{-3} in size. Final atomic positional parameters are given in Table 4; bond lengths and interbond angles (excluding those involving phenyl-group hydrogens) are listed in Table 3.

Crystal data. $C_{23}H_{16}AuCrO_5P$, $M = 651$, triclinic, space group $P\bar{1}$ (no. 2), cell dimensions at 298 K, $a = 9.310(3)$, $b = 12.105(5)$, $c = 11.967(4)$ Å, $\alpha = 112.90(3)$, $\beta = 95.56(4)$, $\gamma = 109.59(3)°$, $U = 1\,129.6(7)$ Å^3; cell dimensions at 210 K, $a = 9.244(5)$, $b = 12.019(8)$, $c = 11.786(6)$ Å, $\alpha = 112.67(4)$, $\beta = 95.90(4)$, $\gamma = 109.81(4)°$, $U = 1\,095(1)$ Å^3, $Z = 2$, $D_c = 1.974$ g cm^{-3}, $F(000) = 624$, $\mu(\text{Mo-}K_\alpha) = 72.68$ cm^{-1}.

Atomic scattering factors for all atoms were taken from ref. 29, and all calculations were performed with programs described in ref. 30.

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