

Note

Synthesis and structure of $[M(CO)_4\{(PPh_2)_2CHAu(PPh_3)\}]$ ($M = Cr, Mo, W$)

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Abstract

The reaction of diethyl ether solutions of $Li[M(CO)_4\{(PPh_2)_2CH\}]$ with $[AuCl(PPh_3)]$ gives $[M(CO)_4\{(PPh_2)_2CHAu(PPh_3)\}]$ ($M = Cr, Mo, W$). The structure of the derivative with $M = Mo$ was determined by single-crystal X-ray diffraction at 173 K. Crystals are monoclinic, space group $P2_1$, $a = 13.552(3)$, $b = 17.718(4)$, $c = 17.390(4)$ Å, $\beta = 90.94(2)^\circ$, $Z = 4$ and $R(F) = 0.031$. The two independent molecules are very similar. The molybdenum and the gold atoms display octahedral and linear geometries, respectively; the shortest intramolecular molybdenum–gold interaction is 4.52 Å.

Keywords: Crystal structures; Gold complexes; Group 6 metal complexes; Tridentate ligand complexes

1. Introduction

It has been reported that the methanide complex $[M(CO)_4\{(PPh_2)_2CH\}]^-$ ($M = Cr, Mo, W$) can be alkylated [1,2] or acylated [3] to give $[M(CO)_4\{(PPh_2)_2CHR\}]$ ($R = Me, Et, CH_2Ph, CH_2CHCH_2, CPh, CO(C_6H_4Me), SiMe_3$ or PPh_2), but no reactions with transition metal complexes have been studied.

In this paper we describe the synthesis of $[M(CO)_4\{(PPh_2)_2CHAu(PPh_3)\}]$ by reaction of $[M(CO)_4\{(PPh_2)_2CH\}]^-$ with $AuCl(PPh_3)$. Although polynuclear complexes with the units $[M'\{(PPh_2)_2CHAu(PPh_3)\}]^{n+}$, $[M'\{(PPh_2)_2C(AuPPh_3)_2\}]^{n+}$ [4–6] or $[M'\{(PPh_2)_2C\}_2-Hg]^{n+}$ [7] have been reported, no examples have been given with the metal center M' in oxidation state zero.

2. Experimental

All reactions were performed at room temperature under a nitrogen atmosphere using freshly dried solvents. The NMR spectra were recorded on a Varian 300 UNITY spectrometer in $CDCl_3$. Chemical shifts are cited relative to $SiMe_4$ (1H) and H_3PO_4 (85%, external, ^{31}P). Mass spectra were recorded on a VG Autospec. The yields, melting points, elemental

analyses, conductivities, $\nu(CO)$ bands and ^{31}P NMR data for the new complexes are listed in Table 1.

2.1. Preparation of the complexes

$[M(CO)_4\{(PPh_2)_2CH(AuPPh_3)\}]$ ($M = Cr$ (1), Mo (2), W (3)). To a solution of $[M(CO)_4\{(PPh_2)_2CH_2\}]$ [8] (0.0548 g (Cr), 0.0592 g (Mo) or 0.068 g (W); 0.1 mmol) in diethyl ether (30 ml) was added $nBuLi$ (1.6 M hexane solution, 0.4 mmol). After stirring for 2 h, $[AuCl(PPh_3)]$ (0.0495 g, 0.1 mmol) was added and the mixture was stirred for 8 h. The solid formed was removed by filtration through a 1 cm layer of diatomaceous earth. The solution was concentrated to ~5 ml, whereupon addition of n-hexane (15 ml) gave an orange (1), yellow (2) or pale yellow (3) solid.

2.2. Crystal structure determination of complex 2

Crystal data. $C_{47}H_{36}AuMoO_4P_3$, $M_r = 1050.57$, monoclinic, space group $P2_1$, $a = 13.552(3)$, $b = 17.718(4)$, $c = 17.390(4)$ Å, $\beta = 90.94(2)^\circ$, $V = 4175(2)$ Å³, $Z = 4$, $D_c = 1.671$ Mg m⁻³, $F(000) = 2064$, $\lambda(Mo K\alpha) = 0.71073$ Å, $\mu = 4.0$ mm⁻¹, $T = -100^\circ C$.

Data collection and reduction. Single crystals of compound 2 in the form of pale yellow prisms were obtained by

Table 1
Analytical and physical data for the complexes

Complex	Yield (%)	Analysis ^a (%)		M.p. (°C)	A_M^b	$\nu(\text{CO})^c$ (cm ⁻¹)	³¹ P NMR ^d (ppm)	
		C	H				$\delta(\text{PPh}_2)$	$\delta(\text{PPh}_3)$
1	74	56.4 (56.1)	3.7 (3.6)	118(dec.)	7	1999(s) 1887(vs,br) 1852(s,br)	35.7(d) [10.9]	40.3(t)
2	90	53.6 (53.75)	3.35 (3.45)	142	3	2013(vs) 1904(vs,br) 1860(vs,br)	12.6 (d) [11.0]	40.3 (t)
3	66	49.9 (49.6)	3.2 (3.2)	130(dec.)	5	2008(s) 1898(vs,br) 1852(vs,br)	-11.9 (d) [11.0]	40.4 (t)

^a Calculated values in parentheses.

^b In acetone at 25 °C, $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

^c In dichloromethane solution.

^d Recorded in CDCl_3 solution referred to external H_3PO_4 , at room temperature. Coupling constants (P–P) in Hz are shown in square brackets; d = doublet, t = triplet.

slow diffusion of n-hexane into a dichloromethane solution. A crystal $\sim 0.45 \times 0.45 \times 0.4$ mm was mounted in inert oil, transferred to the cold gas stream of a Siemens R3 diffractometer, and used to collect 10 559 intensities to $2\theta_{\text{max}} 50^\circ$ (monochromated Mo $K\alpha$ radiation). An absorption correction based on ψ -scans was applied, with transmission factors 0.65–0.96. Merging equivalents gave 7651 independent reflections (R_{int} 0.030). Cell constants were refined from setting angles of 50 reflections in the range 2θ 20–23°.

Structure solution and refinement. The structure was solved by the heavy-atom method and subjected to full-matrix least-squares refinement (program system SHELXL-93 [9]). Atoms heavier than C were refined anisotropically; phenyl rings were idealized. The remaining hydrogen atom was included using a riding model. A pronounced pseudosymmetry was noted; the heavy-atom positions correspond closely to the space group $P2_1/n$. Enantiomeric twinning was assumed, with components 0.675, 0.325(9). Refinement proceeded to $wR(F^2)$ 0.084 for 7336 reflections, 372 parameters

and 133 restraints, conventional $R(F)$ 0.031, S 1.04, max. $\Delta\rho$ 1.1 e $\text{\AA}^{-3}$.

3. Results and discussion

The reaction of $[\text{M}(\text{CO})_4\{(\text{PPh}_2)_2\text{CH}_2\}]$ ($\text{M} = \text{Cr}, \text{Mo}$ or W) with an excess of $^n\text{BuLi}$ leads to solutions of $\text{Li}[\text{M}(\text{CO})_4\{(\text{PPh}_2)_2\text{CH}\}]$, as described elsewhere [1–3]. Addition of the stoichiometric amount (or even an excess) of $[\text{AuCl}(\text{PPh}_3)]$ gives complexes 1–3.

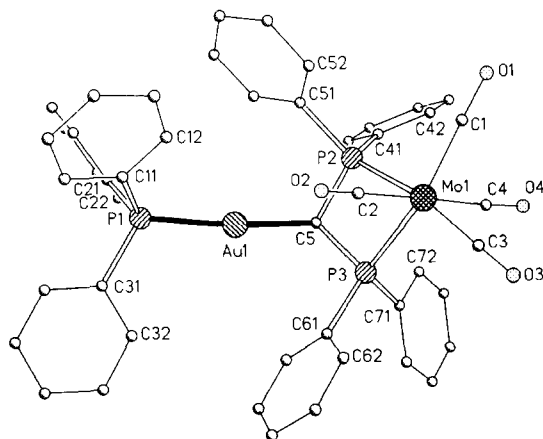
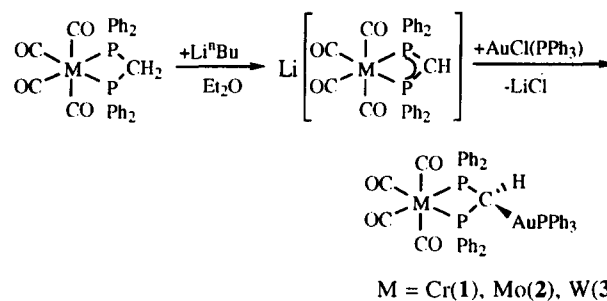


Fig. 1. One of the two independent molecules of compound 2 in the crystal. Radii are arbitrary; H atoms omitted for clarity.

We have recently reported that acetylacetonate (acac) complexes, such as $[\text{Au}(\text{acac})(\text{PPh}_3)]$, are precursors capable of abstracting the proton of the groups $(\text{PPh}_2)_2\text{CH}_2$ or $(\text{PPh}_2)_2\text{CHAu}(\text{PPh}_3)$ and introducing new gold centers [5]; but no reaction was observed between $[\text{M}(\text{CO})_4\{(\text{PPh}_2)_2\text{CH}_2\}]$ or complexes 1–3 and $[\text{Au}(\text{acac})(\text{PPh}_3)]$.

Complexes 1–3 are air- and moisture-stable orange (1), yellow (2) or pale yellow (3) solids and their acetone solutions are non-conducting (Table 1). The positive-ion fast atom bombardment (FAB) mass spectra show the molecular cation peak (M) for complexes 2 or 3 at $m/z = 1052$ (10) or 1139 (15%), respectively. Other peaks appear at $m/z = 894$ (100, $[\text{M}-4\text{CO}]^+$) and 459 (27, $[\text{AuPPh}_3]^+$) for 1, 941 (15, $[\text{M}-4\text{CO}]^+$), 844 (22, $[\text{M}-4\text{CO}-\text{Mo}]^+$) and 459 (100, $[\text{AuPPh}_3]^+$) for 2, and 1027 (5, $[\text{M}-4\text{CO}]^+$),

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for compound 2

	x	y	z	U_{eq}^a
Au(1)	4935.1(2)	6783.6(2)	6773.3(2)	24.8(1)
Mo(1)	2051.8(5)	8168.7(6)	6722.8(4)	24.8(2)
P(1)	6581.9(15)	6835(2)	6533.1(11)	26.2(5)
P(2)	3122(2)	7525.3(14)	7729.7(12)	22.9(5)
P(3)	2535.9(15)	6829(2)	6380.2(11)	24.9(4)
C(1)	1803(7)	9115(6)	7296(6)	38(2)
O(1)	1611(6)	9628(5)	7674(5)	62(2)
C(2)	3299(7)	8578(6)	6218(5)	32(2)
O(2)	3974(5)	8831(5)	5928(4)	49(2)
C(3)	1237(7)	8508(5)	5834(5)	32(2)
O(3)	744(5)	8705(5)	5328(4)	53(2)
C(4)	761(7)	7796(6)	7145(6)	38(2)
O(4)	1(5)	7651(5)	7393(4)	58(2)
C(5)	3465(6)	6723(6)	7146(4)	26(2)
C(11)	7050(4)	7784(3)	6383(3)	27(2)
C(12)	6491(3)	8383(3)	6653(3)	33(2)
C(13)	6846(4)	9117(3)	6600(4)	42(2)
C(14)	7760(5)	9252(3)	6276(4)	47(3)
C(15)	8320(4)	8653(4)	6006(4)	55(3)
C(16)	7965(4)	7920(3)	6060(4)	48(3)
C(21)	7265(4)	6470(3)	7366(3)	26(2)
C(22)	6983(4)	5768(3)	7646(3)	45(2)
C(23)	7464(5)	5464(3)	8286(4)	48(3)
C(24)	8226(5)	5860(4)	8646(3)	39(2)
C(25)	8508(4)	6561(4)	8367(3)	48(3)
C(26)	8027(4)	6866(3)	7726(3)	38(2)
C(31)	6991(4)	6270(4)	5731(3)	34(2)
C(32)	6331(3)	6153(4)	5122(3)	40(2)
C(33)	6623(4)	5747(4)	4481(3)	46(3)
C(34)	7574(5)	5458(4)	4448(3)	44(2)
C(35)	8234(4)	5574(4)	5057(4)	48(3)
C(36)	7943(4)	5980(4)	5698(3)	39(2)
C(41)	2558(4)	7149(3)	8609(3)	28(2)
C(42)	1720(4)	7505(3)	8885(3)	28(2)
C(43)	1235(4)	7208(3)	9515(3)	41(2)
C(44)	1588(5)	6557(4)	9870(3)	48(3)
C(45)	2425(5)	6201(3)	9594(4)	43(2)
C(46)	2910(4)	6498(3)	8964(4)	40(2)
C(51)	4266(3)	7964(3)	8107(3)	26(2)
C(52)	4360(4)	8742(3)	8032(3)	34(2)
C(53)	5216(4)	9100(2)	8291(4)	41(2)
C(54)	5977(3)	8681(3)	8624(3)	39(2)
C(55)	5882(3)	7904(3)	8699(3)	41(2)
C(56)	5027(4)	7545(2)	8441(4)	35(2)
C(61)	3070(4)	6572(3)	5458(2)	29(2)
C(62)	2899(4)	7030(3)	4821(3)	31(2)
C(63)	3246(5)	6817(3)	4105(3)	47(2)
C(64)	3764(5)	6145(4)	4027(3)	46(3)
C(65)	3936(4)	5687(3)	4663(3)	40(2)
C(66)	3589(5)	5900(3)	5379(3)	32(2)
C(71)	1628(4)	6066(3)	6520(3)	30(2)
C(72)	1243(5)	5973(4)	7250(3)	39(2)
C(73)	523(5)	5430(4)	7376(3)	46(3)
C(74)	189(5)	4979(4)	6771(4)	53(3)
C(75)	574(5)	5072(4)	6041(3)	52(3)
C(76)	1293(5)	5615(4)	5916(3)	40(2)
Au(1')	9.2(2)	3194.0(2)	8052.9(2)	25.3(1)
Mo(1')	2872.4(5)	1957.8(5)	8542.2(4)	26.1(2)
P(1')	-1657(2)	3024.5(14)	8166.9(13)	26.0(5)
P(2')	2264.4(15)	3289.4(15)	8757.0(11)	24.4(5)

(continued)

844 (5, $[M-4CO-W]^+$), 680 (18, $[W(CO)_4\{(PPh_2)_2CH\}]^+$) and 459 (30%, $[AuPPh_3]^+$) for 3.

Their IR spectra in CH_2Cl_2 solution show three bands for the terminal CO groups (Table 1), characteristic of *cis*-tetra-carbonyl derivatives and in agreement with observations for other *cis*- $[M(CO)_4L_2]$ complexes [10]. The $^{31}P\{^1H\}$ NMR spectra (Table 1) show two different phosphorus environ-

Table 2 (continued)

	x	y	z	U_{eq}^a
P(3')	2068(2)	2558.2(14)	7376.1(12)	23.6(5)
C(1')	3454(8)	1621(6)	9547(6)	45(3)
O(1')	3823(7)	1406(5)	10106(5)	69(3)
C(2')	1591(7)	1475(6)	8898(6)	37(2)
O(2')	914(5)	1186(6)	9141(5)	60(3)
C(3')	3339(8)	1040(6)	8029(6)	41(2)
O(3')	3658(7)	524(5)	7692(6)	72(3)
C(4')	4196(7)	2429(6)	8323(6)	40(2)
O(4')	4952(5)	2692(5)	8243(5)	64(2)
C(5')	1521(6)	3372(5)	7876(4)	21(2)
C(11')	-1973(4)	2030(3)	8090(4)	30(2)
C(12')	-2950(4)	1793(3)	8045(3)	33(2)
C(13')	-3170(4)	1027(4)	8032(4)	52(3)
C(14')	-2414(5)	498(3)	8065(4)	57(3)
C(15')	-1437(4)	735(3)	8111(4)	44(3)
C(16')	-1217(3)	1501(3)	8123(4)	41(2)
C(21')	-2147(4)	3404(3)	9060(3)	24(2)
C(22')	-1624(3)	3991(3)	9406(3)	31(2)
C(23')	-1994(4)	4346(3)	10053(3)	40(2)
C(24')	-2888(4)	4115(3)	10354(3)	40(2)
C(25')	-3412(3)	3528(4)	10008(3)	39(2)
C(26')	-3041(4)	3172(3)	9362(3)	31(2)
C(31')	-2373(4)	3471(3)	7393(2)	23(2)
C(32')	-1922(3)	3568(4)	6687(3)	29(2)
C(33')	-2454(4)	3866(4)	6069(2)	40(2)
C(34')	-3438(4)	4068(4)	6155(3)	37(2)
C(35')	-3889(3)	3971(4)	6861(3)	35(2)
C(36')	-3356(4)	3673(4)	7479(2)	30(2)
C(41')	3239(4)	4018(3)	8728(3)	24(2)
C(42')	3514(4)	4376(3)	8053(2)	29(2)
C(43')	4299(4)	4880(3)	8062(3)	38(2)
C(44')	4809(4)	5027(3)	8746(3)	39(2)
C(45')	4534(4)	4669(4)	9421(3)	48(3)
C(46')	3749(4)	4165(4)	9412(2)	39(2)
C(51')	1558(4)	3642(3)	9570(3)	28(2)
C(52')	1442(4)	3181(3)	10209(3)	38(2)
C(53')	913(5)	3438(4)	10834(3)	53(3)
C(54')	500(5)	4156(4)	10822(3)	49(3)
C(55')	616(5)	4617(3)	10183(4)	47(3)
C(56')	1145(5)	4360(3)	9557(3)	35(2)
C(61')	1107(4)	2066(3)	6804(3)	29(2)
C(62')	940(4)	1308(3)	6962(3)	37(2)
C(63')	193(5)	921(3)	6573(4)	48(3)
C(64')	-389(4)	1292(4)	6026(4)	45(3)
C(65')	-223(4)	2050(4)	5868(3)	56(3)
C(66')	525(5)	2437(3)	6257(3)	38(2)
C(71')	2844(4)	2952(3)	6612(3)	27(2)
C(72')	2576(4)	3605(3)	6218(3)	31(2)
C(73')	3164(4)	3875(3)	5631(3)	39(2)
C(74')	4020(4)	3492(4)	5438(3)	40(2)
C(75')	4288(4)	2838(4)	5832(4)	47(3)
C(76')	3700(4)	2568(3)	6419(3)	34(2)

^a U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3

Selected bond lengths (Å) and angles (°) for compound 2. The second columns correspond to the second (primed) molecule

Au(1)–C(5)	2.108(8)	2.101(8)	Au(1)–P(1)	2.279(2)	2.289(2)
Mo(1)–C(1)	1.982(11)	1.997(11)	Mo(1)–C(2)	2.050(9)	2.041(11)
Mo(1)–C(3)	1.978(9)	1.965(11)	Mo(1)–C(4)	2.019(10)	2.020(10)
Mo(1)–P(2)	2.527(2)	2.529(3)	Mo(1)–P(3)	2.537(3)	2.522(2)
P(1)–C(11)	1.818(5)	1.818(5)	P(1)–C(21)	1.825(5)	1.828(4)
P(1)–C(31)	1.812(5)	1.827(4)	P(2)–C(5)	1.811(10)	1.825(8)
P(2)–C(41)	1.846(5)	1.847(5)	P(2)–C(51)	1.845(4)	1.830(5)
P(3)–C(5)	1.828(8)	1.845(8)	P(3)–C(61)	1.828(4)	1.846(5)
P(3)–C(71)	1.847(5)	1.845(5)			
C(5)–Au(1)–P(1)	172.6(2)	176.4(2)	C(1)–Mo(1)–C(2)	93.7(4)	86.3(4)
C(1)–Mo(1)–C(3)	92.2(4)	91.4(4)	C(1)–Mo(1)–C(4)	86.5(4)	87.1(4)
C(1)–Mo(1)–P(2)	97.7(3)	105.9(3)	C(1)–Mo(1)–P(3)	163.1(3)	171.5(3)
C(2)–Mo(1)–C(3)	90.6(4)	94.1(4)	C(2)–Mo(1)–C(4)	175.3(4)	173.1(4)
C(2)–Mo(1)–P(2)	89.3(3)	93.7(3)	C(2)–Mo(1)–P(3)	90.7(3)	93.5(3)
C(3)–Mo(1)–C(4)	84.7(4)	87.9(4)	C(3)–Mo(1)–P(3)	170.1(3)	161.4(3)
C(3)–Mo(1)–P(3)	104.2(3)	97.0(3)	C(4)–Mo(1)–P(2)	95.3(3)	86.2(3)
C(4)–Mo(1)–P(3)	90.5(3)	92.7(3)	P(2)–Mo(1)–P(3)	65.97(7)	65.65(7)
C(11)–P(1)–C(21)	105.6(3)	109.3(3)	C(11)–P(1)–C(31)	106.8(3)	104.1(3)
C(21)–P(1)–C(31)	104.9(3)	105.7(3)	C(11)–P(1)–Au(1)	114.1(2)	110.7(2)
C(21)–P(1)–Au(1)	109.0(2)	113.5(2)	C(31)–P(1)–Au(1)	115.6(2)	113.1(2)
C(5)–P(2)–C(41)	107.1(4)	107.8(3)	C(5)–P(2)–C(51)	108.0(3)	109.4(3)
C(5)–P(2)–Mo(1)	96.6(3)	97.3(3)	C(41)–P(2)–C(51)	102.4(3)	99.5(3)
C(41)–P(2)–Mo(1)	119.7(2)	114.4(2)	C(51)–P(2)–Mo(1)	121.7(2)	127.5(2)
C(5)–P(3)–C(61)	109.6(3)	109.7(3)	C(5)–P(3)–C(71)	106.4(4)	106.4(3)
C(5)–P(3)–Mo(1)	95.9(4)	97.0(3)	C(61)–P(3)–C(71)	102.0(3)	101.3(3)
C(61)–P(3)–Mo(1)	123.1(2)	121.7(2)	C(71)–P(3)–Mo(1)	118.6(2)	119.7(2)
P(2)–C(5)–P(3)	98.5(5)	96.5(4)	P(2)–C(5)–Au(1)	112.7(5)	113.0(4)
P(3)–C(5)–Au(1)	114.4(4)	110.6(4)			

ments, which appear as a doublet and a triplet for the PPh_2 and AuPPh_3 groups, respectively. The upfield resonance of complex **3** possesses tungsten satellites with $J(\text{PW}) = 96.3$ Hz. The substitution of a proton for $[\text{AuPPh}_3]^+$ in $[\text{M}(\text{CO})_4\{(\text{PPh}_2)_2\text{CH}_2\}]$ leads to a slight displacement of the PPh_2 resonances to high field ($\Delta = 10$ ppm). The ^1H NMR spectra show pseudoquartets for the methine protons at 5.20 (1), 5.24 (2) or 6.09 (3) ppm ($J(\text{H}-\text{PPh}_2) = J(\text{H}-\text{PPh}_3) = 9$ Hz), indicating that the CH proton is less shielded than in the starting product ($\delta \sim 4.5$).

The crystal structure of complex **2** has been established by X-ray crystallography. There are two molecules in the asymmetric unit; one of these is shown in Fig. 1, with atomic coordinates in Table 2 and selected bond lengths and angles in Table 3. The two molecules display similar dimensions, but differences of up to 9° are observed in some angles at the octahedrally coordinated molybdenum atoms. The main distortions from ideal geometry arise from the restricted bite of the diphosphine, $\text{P}(2)\text{--Mo}(1)\text{--P}(3)$ $65.97(7)$, $65.65(7)^\circ$ (values for both independent molecules). This bite angle is smaller than that in the starting material $[\text{Mo}(\text{CO})_4\{(\text{PPh}_2)_2\text{CH}_2\}]$ [11] ($67.3(1)^\circ$) and those in other complexes containing chelated $\text{Ph}_2\text{PCH}_2\text{PPh}_2$, where the P--M--P angles range from 67 to 74° [12]. The chelate ring formed by $\text{Mo}(1)$, $\text{P}(2)$, $\text{P}(3)$ and $\text{C}(5)$ is approximately planar, but is folded about the P...P axis by 17.8 (19.1) $^\circ$; the molybdenum atom lies 0.045 (0.064) Å out of the plane formed by $\text{P}(2)\text{--P}(3)\text{--C}(1)\text{--C}(3)$. There are two slightly different

ranges of Mo--CO bond distances; the shortest ($1.965\text{--}1.997$ Å) are to the carbonyl groups *trans* to the phosphorus atoms, whereas the distances to the *cis* carbonyls are $2.019\text{--}2.050$ Å. The Mo--P bond lengths are $2.527(2)\text{--}2.537(3)$ Å, of the same order as in the starting complex $[\text{Mo}(\text{CO})_4\{(\text{PPh}_2)_2\text{CH}_2\}]$ ($2.535(3)$ and $2.501(2)$ Å). The coordination at the gold atom is slightly distorted from linear, with an angle $\text{C}(5)\text{--Au}(1)\text{--P}(1)$ $172.6(2)$, $176.4(2)^\circ$. The intramolecular Mo...Au distances are 4.61 , 4.52 Å.

4. Supplementary material

Full details of the structure determination have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-technische Information mbH, 76344 Eggenstein-Leopoldshafen, Germany, from where this material can be obtained on quoting the full literature citation and the reference number CSD 401638.

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