Novel gold derivatives of titanium carbonyl and structural characterization of a compound containing an unsupported gold–titanium bond: $[Ti(CO)_6(AuPEt_3)]^-$†

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Hexacarbonyltitanate(2−) reacts with $(R_3P)AuCl$ (R = C_6H_{11}, Et) to provide the first anions of the general formula $[M(CO)_x(AuPR_3)_y]^z$, and a structurally characterized (for R = Et) compound containing a largely unsupported gold–titanium bond.

Mixed gold–transition metal compounds have been known for over thirty years[1] and now hold a special position in chemistry by virtue of their often intriguing chemical and physical properties.[2] While structurally characterized compounds containing gold–metal bonds are well known for most transition-metal elements, the first example containing titanium was reported only very recently, an unusual bis(alkynyl)titanocene-gold aryl adduct; $[\{(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2\}\text{-}Au\{C_6H_2(CF_3)_3\text{-}1,3,5\}]$ **1**.[3] Since the gold atom in this complex was strongly bound to the two alkyne groups, it was required to be in close proximity to the formally Ti^{IV} center. To assess whether the gold–titanium interaction was significant, as claimed,[3] we felt that it was important to obtain and determine the molecular structure of a compound containing a largely unsupported gold–titanium bond. Numerous attempts to prepare the unknown carbonyltitanate $[Ti(CO)_6(AuPPh_3)]^-$, which is analogous to the well established vanadium complex $[V(CO)_6(AuPPh_3)]$,[4,5] by the reaction of $[Ti(CO)_6]^{2-}$ with $(Ph_3P)AuCl$ were uniformly unsuccessful. However, dropwise addition of cold (−50 to −60 °C) solutions of $(R_3P)AuCl$, (R = C_6H_{11}, Et) to an equimolar quantity of $[K(15\text{-crown-}5)_2]_2[Ti(CO)_6]$,[6] as a finely divided cold (−50 to −80 °C) solid, provided 20–35% isolated yields of satisfactorily pure $[K(15\text{-crown-}5)_2][Ti(CO)_6(AuPR_3)]$ (R = C_6H_{11} **2a**, Et **2b**), Scheme 1.‡

Compounds **2a,b** are air-sensitive brown to red–brown microcrystalline solids. Both have nearly identical IR spectra in the ν(CO) region in thf, which indicates that the carbonyl products have very similar molecular structures in solution. Carbon-13 NMR spectra of these species in thf are also very similar and show a single carbonyl resonance at δ_C *ca.* 250 from 25 to −90 °C. To confirm the presence of seven-coordinate titanium in **2a**, a 99% ^{13}CO enriched sample was prepared from the known $[Ti(^{13}CO)_6]^{2-}$ [6] by the same procedure. The ^{13}C and ^{31}P NMR spectra of $[^{13}C_6]$**2a** showed the expected doublet (δ_C, +250.3, $^3J_{PC}$ 5 Hz) and a well resolved binomial septet (δ_P, 74.3, $^3J_{PC}$ 5 Hz), respectively, arising from coupling of the six equivalent carbonyl carbons to phosphorus in the coordinated tricyclohexylphosphine group. The equivalence of the carbonyl groups undoubtedly arises from the highly fluxional nature of **2a** in solution. Attempts to grow X-ray quality crystals of **2a** were unsuccessful, but suitable single crystals of **2b** were obtained.§

$$[Ti(CO)_6]^{2-} + (R_3P)AuCl \xrightarrow[-60\text{ to }0\ ^\circ C]{\text{thf}} [Ti(CO)_6(AuPR_3)]^- + Cl^-$$

$$(R = C_6H_{11},\ Et)$$

Scheme 1

The anion in **2b** (Fig. 1) has an irregular seven-coordinate geometry about titanium. A view down the Ti–Au vector shows an approximate capped trigonal prism, where gold 'caps' carbonyl carbons C(1–4); however, the latter define a substantially non-planar face. The C(1)–Ti–C(2) and C(3)–Ti–C(4) angles of 123.1(3) and 167.1(3)°, respectively, deviate markedly from that expected for an undistorted capped trigonal prism.[7] The origin of this severe distortion is a close approach of one CO group, defined by C(1), to the gold atom. Although the Au–C(1) distance of 2.416(8) Å is outside the range of normal Au–C bond lengths and is significantly longer than the average Au–C(η^2-alkyne) value of 2.23 (1) Å found in complex **1**, other structural and spectral data for crystalline **2b** point to the presence of a very weak 'semibridging' carbonyl–gold interaction. For example, the C(1)–O(1) and Ti–C(1) distances are significantly longer and shorter, respectively, than the other corresponding distances in **2b**, except that for Ti–C(4) (Fig. 1). Also, the slight non linearity of the Ti–Au–P angle of 169.45(6)° and a difference in the solid-state and solution IR spectra of **2b** in the ν(CO) region suggest that this interaction is present. Specifically, the lowest-energy ν(CO) band of **2b** decreases from 1814 cm^{-1} in solution to 1791 cm^{-1} as a mulled solid, which is the trend expected for a weak interaction of this type.[8] By comparison, the shortest carbonyl carbon–gold distance in the closely related $[V(CO)_6(AuPPh_3)]$ is 2.57(2) Å.[5] For the latter complex, there is no IR spectral evidence for any analogous Au–CO interaction in the solid state.[9] The average Ti–C and C–O distances are 2.05(1) and 1.16(1) Å, respectively, which are similar to corresponding values of 2.04(1) and 1.16(2) Å found in a related Ti^0 anionic carbonyl $[Ti(CO)_5(SnPh_3)_2]^{2-}$.[10] The Au–P distance in **2b** of 2.295(2) Å is similar to those found in other triethylphosphine gold–metal

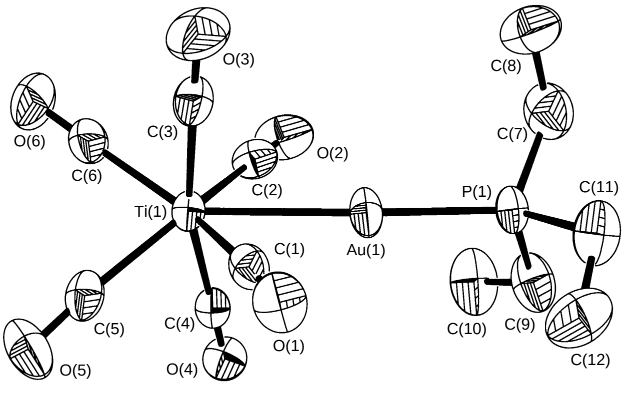

Fig. 1 Molecular structure of the anion in **2b**. Selected dimensions (Å and °): Ti–C(1) 2.034(9), Ti–C(2) 2.065(9), Ti–C(3) 2.056(9), Ti–C(4) 2.046(8), Ti–C(5) 2.053(9), Ti–C(6) 2.060(9), Ti–Au 2.719(1), Au–P 2.295(2), Au–C(1) 2.416(8), Au–C(2) 2.599(8), C(1)–O(1) 1.175(9), C(2)–O(2) 1.141(9), C(3)–O(3) 1.155(9), C(4)–O(4) 1.155(9), C(5)–O(5) 1.147(10), C(6)–O(6) 1.155(9), P–C(av.) 1.81(1), C–C(av.) 1.48(2); Ti–Au–P 169.45(6), Ti–C(1)–O(1) 173.7(7), Ti–C(2)–O(2) 174.0(8), other Ti–C–O (av.) 177(2).

complexes; *e.g.* in $[Os_3(CO)_{10}(AuPEt_3)_2]$ the distance is 2.287(6) Å.[11] More interesting is the Ti–Au bond length of 2.719(1) Å, which, as expected, is slightly longer than the V–Au distance of 2.690(3) Å in $[V(CO)_6(AuPPh_3)]$,[5] but is 0.276 Å shorter than the Ti–Au separation of 2.995(1) Å reported for compound **1**. On this basis, although the existence of a Ti–Au bond in **1** cannot be ruled out, it is undoubtedly much weaker than that present in $[Ti(CO)_6(AuPEt_3)]^-$. The counter ion in **2b**, $[K(15\text{-crown-}5)_2]^+$, is well separated from anions in the crystalline lattice and has the usual sandwich structure containing formally ten-coordinate potassium ion, with a mean K–O distance of 2.89(5) Å. The latter number is essentially identical to the corresponding value of 2.88(9) Å, recently found in $[K(15\text{-crown-}5)_2][Zr(CO)_4(dppe)(SnMe_3)]$.[12]

Compounds **2a,b** are of additional interest in that they contain the first known anionic complexes of the general formula $[M(CO)_x(AuPR_3)_y]^z$ and may be regarded as structural models[13,14] for the presently unknown hydride, $[Ti(CO)_6H]^-$. All previously reported reactions of homoleptic carbonylmonometalates, *i.e.*, $[M(CO)_x]^{y-}$, with phosphine gold halides have given only neutral compounds of the type $[M(CO)_x(AuPR_3)_y]$. For example, the reaction of $[V(CO)_5]^{3-}$ with fewer than 3 equiv. of $(Ph_3P)AuCl$ invariably gave only the neutral gold cluster species $[V(CO)_5(AuPPh_3)_3]$ and unreacted $[V(CO)_5]^{3-}$.[15] Similar unsuccessful attempts to prepare the still unknown $[Fe(CO)_4(AuPPh_3)]^-$ by the reaction of $[Fe(CO)_4]^{2-}$ with 1 equiv. of $(Ph_3P)AuCl$ yielded only the neutral bis-gold complex, $[Fe(CO)_4(AuPPh_3)_2]$.[16] Very likely the pronounced tendency for $(R_3P)Au$ groups to bind to one another and form Au–Au bonds,[2] a phenomenon recently dubbed 'aurophilicity',[17] accounts for the favored formation of the neutral polygold–metal species in these prior studies. The relatively crowded anionic $Ti(CO)_6$ unit in **2a,b** undoubtedly inhibits attack by a second phosphine gold chloride and may be one reason why we were successful for the first time in obtaining substituted metal carbonyl anions of this type. However, substitution of trialkylphosphinegold chlorides in these reactions for the doubtlessly more electrophilic triphenylphosphinegold chloride may also have been of critical importance in this study. Extensions of this research to zirconium and hafnium will be of interest since well characterized gold derivatives of these metals are presently unknown.

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Footnotes

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† Highly Reduced Organometallics 40; Part 39, see ref. 12.

‡ A cold (−50 °C) solution of $[(C_6H_{11})_3P]AuCl$ (0.504 g, 0.984 mmol) in thf (50 ml) was added by cannula to cold (−50 °C) and finely divided solid $[K(15\text{-crown-}5)_2]_2[Ti(CO)_6]$ (1.15 g, 0.982 mmol) with stirring. The resulting red–brown reaction mixture was stirred for 14 h while slowly warming to 0 °C. Following filtration at 0 °C, all but about 5 ml of the solvent was removed *in vacuo*. Addition of excess diethyl ether caused precipitation of the brown solid, which was recrystallized from thf–ether to provide 0.406 g (35% yield) of pure **2a**. Satisfactory elemental analysis. IR(thf): ν(CO) 1951 m, 1918 m, 1811 s cm^{-1}. IR (Nujol): 1959 m, 1922 (sh), 1870 (sh), 1835 (sh), 1780 s, (br) cm^{-1}. ^1H NMR (300 MHz, $[^2H_8]$thf 25 °C, $SiMe_4$): δ 3.53 (s, 40 H, 15-crown-5), 2.5-1.8 [m, 33 H, $AuP(C_6H_{11})_3$]. $^{13}C\{^1H\}$(75 MHz): δ 250.2 (d, $^3J_{PC}$ 4.6 Hz, CO), 69.7 (s, 15-crown-5), 34.3 (d, $^1J_{PC}$ = 17 Hz, C_6H_{11}), 31.2 (d, $^2J_{PC}$ 3 Hz, C_6H_{11}), 28.3 (d, $^3J_{PC}$ 11 Hz, C_6H_{11}), 27.1 (s, C_6H_{11}) ^{31}P (121 MHz, ref. H_3PO_4): δ 74.3 [s, $AuP(C_6H_{11})_3$]. Pure **2b** was obtained by a nearly identical procedure in 20% yield. IR (THF): ν(CO) = 1954m, 1918w, 1814s cm^{-1}. IR (Nujol): 1954m, 1838 (sh), 1791s cm^{-1}. ^1H NMR (300 MHz, $[^2H_8]$thf, 0 °C, $SiMe_4$): δ 3.53 (s, 40 H, 15-crown-5), 1.61 (m, 6 H, $P\mathbf{C}\mathit{H}_2CH_3$), 1.09 (dt, J 7.5, $^3J_{PH}$ = 18 Hz, 9 H , $PCH_2\mathbf{C}\mathit{H}_3$). $^{13}C\{^1H\}$(75 MHz): δ 249 (s, CO), 69.4 (s, 15-crown-5), 20.0 (d, J_{PC} 20 Hz, $P\mathbf{C}\mathit{H}_2CH_3$), 9.5 (d, $^2J_{PC}$ 4.5 Hz, $PCH_2\mathbf{C}\mathit{H}_3$). ^{31}P (121 MHz, ref H_3PO_4) 56.8 [br s $AuP(C_2H_5)_3$].

§ *Crystal data* for **2b**: $C_{32}H_{55}AuKO_{16}PTi$, M = 1010.7, monoclinic, space group $P2_1/c$, a = 14.5279(3), b = 15.8275(1), c = 18.7076(3) Å, β = 93.559(1)°, U = 4293.3(1) $Å^3$, Z = 4, D_c = 1.564 g cm^{-3}, $F(000)$ = 2040, μ(Mo-Kα) = 3.796 mm^{-1}, λ = 0.71073Å, T = 173(2) K. 18 549 reflections measured on a Siemens SMART CCD area detector diffractometer yielded 7415 unique data ($2\theta_{max}$ = 50°, R_{int} = 0.0350, semiempirical absorption corrections). The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2 with statistical weighting, anisotropic displacement parameters, constrained isotropic H atoms to give $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ = 0.1213 on all data, conventional R = 0.0531 on F values of 4965 reflections having $F_o^2 > 2\sigma(F_o^2)$, goodness of fit S = 1.020 for all F^2 values and 472 refined parameters. Largest difference peak and hole: 0.984, −1.063 e $Å^{-3}$. All calculations were performed using SGI INDY R4400-SC or pentium computers with SHEXTL-Plus V5.0 program suite. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/489.

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