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Preliminary communication

First examples of acylgold(I) complexes $RCOAuPPh_3$ (R = Me, *n*-Bu, *t*-Bu, Ph) trapped as oxygen coordinated ligands L at one of rhenium atoms in $Re_2(\mu\text{-}PPh_2)_2(CO)_7(ax\text{-}L)$

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Abstract

In chloroform solution, the title compounds have been generated at room temperature from 1 equiv. $ClAuPPh_3$ and the lithium salts of the type $Li[Re_2(\mu\text{-}PPh_2)_2(CO)_7(ax\text{-}C(R)O)]$ (R = alkyl and aryl residues). The selective formation of such monoanions in the lithium salts from $Re_2(\mu\text{-}PPh_2)_2(CO)_8$ and 1 equiv. LiR in THF solution at −90°C runs quantitatively. All the products obtained were characterized by means of ^1H NMR, ^{31}P NMR and $\nu(CO)$ IR measurements. The molecular structure of $Re_2(\mu\text{-}PPh_2)_2(CO)_7(ax\text{-}n\text{-}BuCOAuPPh_3)$, which has been determined by a single-crystal X-ray analysis, is presented. Such examinations ascertain the first acylgold(I) complexes which are trapped as O-coordinated ligand L in $Re_2(\mu\text{-}PPh_2)_2(CO)_7(ax\text{-}L)$. The unusal transfer of an acyl group from a rhenium to a gold center is discussed. Up to now, our attempts to gain the free acylgold(I) organyls remained unsuccessful. © 1998 Elsevier Science S.A.

Keywords: Acylgold(I) organyls as ligands; Dirhenium complexes; Selective attack of nucleophile

1. Introduction

Gold(I) organyls of the type RAuL may contain a variety of organic residues R as alkyl, vinyl, alkynyl or aryl and as neutral donor ligand L mainly tertiary phosphine, isocyanide and others. [1–7]. Functionalized alkyl and related ligands R like $R = CX_3$ (X = Cl [8], and F [9,10]), CH_2CN, CCl_2CN [11], $CH(CN)(CO_2Et)$ [12,13], $CH(SiMe_3)_2$ [14], $C[NC_6H_3Me_2\text{-}2,6](CH_2COPh)$ [15] and $C[N\text{-}p\text{-}C_6H_4Me](OMe)$ [16,17] have also been synthesized. From the last-named two residues R, it is striking that a sp^2 carbon atom in presence of an imino group attached at triphenylphosphinegold(I) affords thermally stable gold(I) organyls (m.p. > 150°C). However, to our present knowledge, no gold(I)acyl complex is reported in the literature. We describe here a synthetic route to gain the first examples of acylgold(I) complexes.

In general, gold(I) organyls are of manifold interest, namely, to get insight into the nature of bonding in low-valent gold clusters and in gold(I) clusters displaying 'aurophilic' gold–gold interactions with the help of theoretical and spectroscopic studies [18–20], to develop so called carbon-centered systems with multiple tertiary phosphine gold(I) groups [21], to obtain precursors for the chemical vapor deposition of gold films [22], and to determine factors of influence on the stability of gold(I) organyls.

2. Results and discussion

2.1. Preparations

In THF solution, the edge-bridged bioctahedron complex $Re_2(\mu\text{-}PPh_2)_2(CO)_8$ reacts with 1 equiv. of LiR at −90°C to the monoanions of the type $Re_2(\mu\text{-}PPh_2)(CO)_7(ax\text{-}C(R)O]^-$ (R = *n*-Bu **1a**, *t*-Bu **1b**, Me **1c**, Ph **1d**) which are isolable as lithium salts. The designated attack of the nucleophil R^- is directed, therefore, exclusively on one of the four axial and none of the equatorial carbonyl ligands. As only monoanion (C_1 symmetry) formed, it demands one ^{31}P NMR resonance signal as observed. Consequently, the axial addi-

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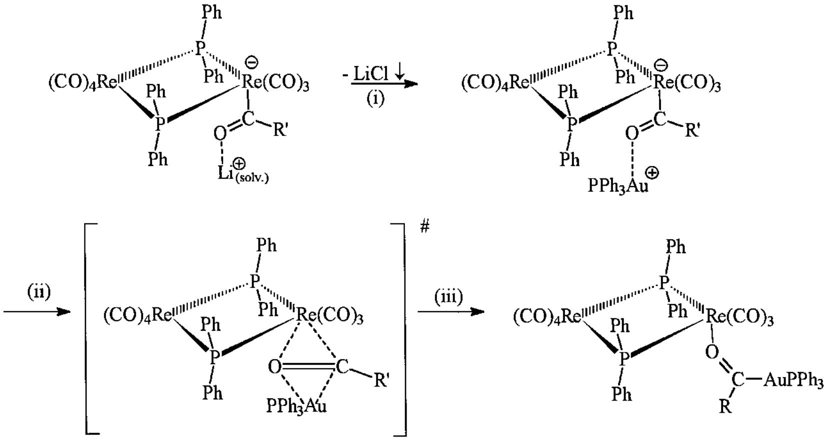

Scheme 1. Proposed reaction pathway.

tion of R^- runs selectively under the present experimental conditions. To the corresponding lithium salts **1a–c** in chloroform solution, 1 equiv. of $ClAuPPh_3$ is added to obtain the title compounds $Re_2(\mu\text{-}PPh_2)_2(CO)_7(ax\text{-}RC(O)AuPPh_3)$ (R = *n*-Bu **2a**, *t*-Bu **2b**, Me **2a**, Ph **2d** Scheme 1). Through a TLC separation procedure, the products **2a–d** were obtained as air-stable, yellow solids yielding 60–70% (**2a, 2c–d**) and 30% (**2b**). The characterization of **2a–d** was done by means of ν(CO)IR, ^1H and ^{31}P NMR measurements and, additionally, by single-crystal X-ray analyses for **2a** (Fig. 1) and **2d** [1] as representatives of this series. Such results confirm that the reaction occurs under maintenance of the axially positioned reaction site in the bioctahedron. The ^{31}P NMR signal of the ligand PPh_3 attached to the gold(I) appears as singlet between 39 and 40 ppm and shows no remarkable change with the R residues. For the carbonyl ligands in the fragment $Re_2(\mu\text{-}PPh_2)_2(CO)_7$, seven ν(CO) absorption modes are present. The ν(CO) mode of the acyl group is situated in the expected region, varying from 1508 cm^1 for **2d** to 1549 cm^{-1} for **2a**.

In Scheme 1, the proposed reaction pathway between the monoanions and $ClAuPPh_3$ is illustrated. Herewith, the reaction step (i) is initiated by a cationic exchange reaction between Li^+ and $AuPPh_3^+$ under formation of the hypothetical ion pair complex $AuPPh_3^+[Re_2(\mu\text{-}PPh_2)_2(CO)_7(C(R)O)]^-$ and of the precipitate LiCl. The gold(I) counter ion as Lewis acid then demands the realization of an additional coordinative bond to diminish the present valence electron deficit (steps ii–iii). To support this proposed reaction pathway, separate experiments were carried out to know the intermediate products formed. They demonstrate the completion of the reaction if the reactants are brought together in a chloroform solution yielding the final yellow color of the title compound which was further controlled by means of ^{31}P NMR measurements. Going from (ii) to (iii), the intramolecular conversion produces, therefore, L in a rapid reaction from the groups $AuPPh_3$ and RC(O) to remove the previous charge separation. The formation of the two-electron ligand L can only be rationalized by a thermodynamically favored change of a Re–C(acyl) to a Re–O(acyl) bond and the formation of a Au–C(acyl) bond. As this pathway is centered around an acyl group, a η^2-acyl bonding pattern can be assumed as transition state [23].

2.2. Structural description

The molecular structure of **2a** as solid (Fig. 1; pertinent crystallographic data are given in Table 1, selected bond lengths and angles in Table 2) confirms the gold-acylation for L = *n*-$BuC(O)AuPPh_3$ together with the aforementioned axial coordination of this ligand at the Re(2) atom of the central Re_2P_2 ring. The latter is nearly planar with a dihedral angle ReP_2/P_2Re of 4.6°. Equatorial and axial CO ligands at the Re atoms are not in fully eclipsed position, with the resulting average torsion angles of 10.9 and 10.7°, respectively. These deformations, however, are not associated with the substitution of a CO ligand vs. the $RC(O)AuPPh_3$ group, as the unsubstituted complex $Re_2(CO)_8(\mu\text{-}PPh_2)_2$ [24] exhibits almost the same geometry. The last-named O-coordinated gold(I)acyl ligand has the typical linear two fold coordination for gold(I) complexes in accordance with the C(7)–Au–P(3) bond angle of 178.6(3)°. The bond angles of the C(7) atom in the acyl group do not differ from those of a C atom embedded as sp^2 hybrid Au–C(7)–C(81) 120.5(8)° and O(7)–C(7)–Au 123.4(8)°. The oxygen coordination of the acyl group shows a Re–O bond length of 2.176(7) Å which corresponds with a σ bond compared to those values of 2.176(7) Å in $Re(CO)_4$ (η^1-$OCOC{\equiv}CH$)($C(NHPr^i)(NHPh)$) and of 2.143(4) Å in *trans*-

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[1] U. Flörke, H.-J. Haupt, D. Petters, unpublished results.

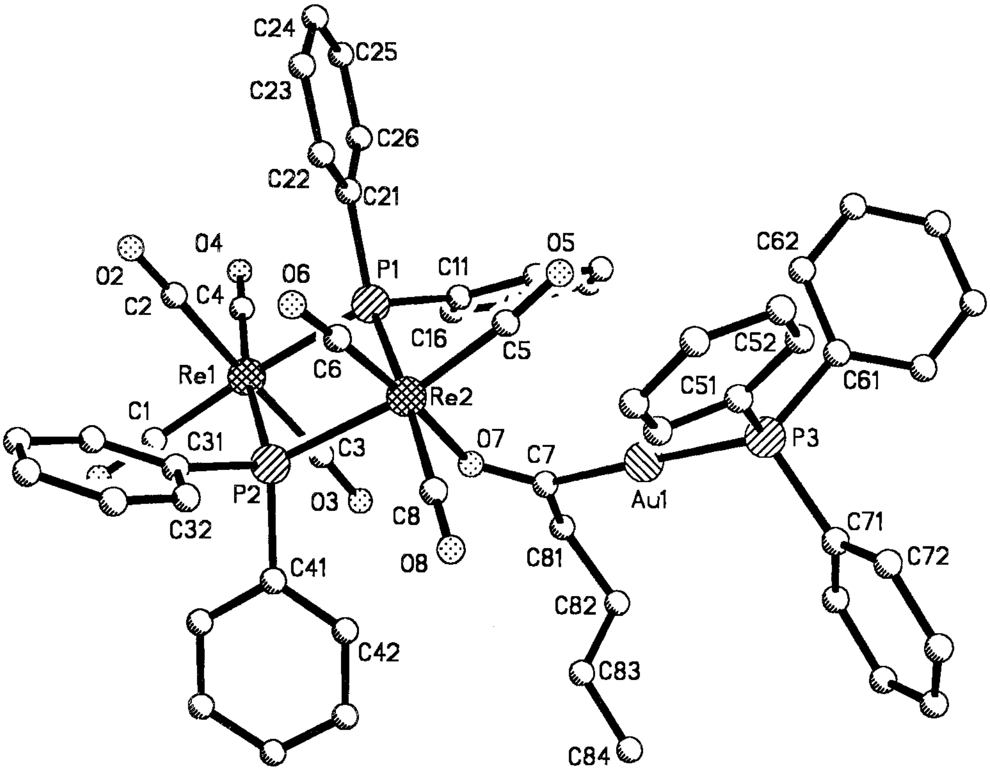

Fig. 1. Molecular structure of **2a**. Hydrogen atoms omitted for clarity.

$Re^{I}(CO)_2(psal)(PMe_2Ph)_2$ (psal = N-phenylsalicylideneaminate) [25,26]. The σ Au–C bond length of 2.047(11) Å is also in the expected range for this type of C atom, comparable to the related carbon atom with a Au–C bond length of 2.056(16) Å in $PPh_3AuC(OMe)(N(p\text{-}C_6H_4Me)$ [16,17]. Furthermore, the Au–P bond length of 2.292(5) Å from this latter compound agrees well with that of 2.301(3) Å in the newly prepared compound. Such analogous structural facts are a hopeful indication to gain a free acylgold(I) complex in the future.

Table 1
Crystal data and refinement details for **2a**

Formula	$C_{54}H_{44}AuO_8P_3Re_2 \cdot CHCl_3$
M_w	1602.5
Crystal system	triclinic
Space group	P-1
a (Å)	11.919(2)
b (Å)	13.921(3)
c (Å)	18.535(5)
α (°)	84.06(2)
β (°)	80.50(2)
γ (°)	69.65(2)
V (Å^3)	2840(1)
Z	2
D_c (g cm^{-3})	1.874
μ (mm^{-1})	7.10
F (000)	1528
Diffractometer	Siemens R3m
Radiation	Mo Kα
Scan type	ω, $4 \le 2\Theta \le 55°$
$R1$, $wR2$	0.062, 0.133

3. Experimental

All reactions were performed with standard Schlenk techniques in solvents free of oxygen which were dried according to literature methods, distilled and stored under argon atmosphere. The reaction products were characterized by υ(CO) FTIR spectroscopy (Nicolet P510), ^{1}H and ^{31}P NMR spectroscopy (Bruker WR 300).

Table 2
Selected bond lengths (Å) and angles (°) for **2a**

Au(1)–C(7)	2.047(11)
Au(1)–P(3)	2.301(3)
Re(1)–P(1)	2.522(3)
Re(1)–P(2)	2.511(3)
Re(2)–P(1)	2.524(3)
Re(2)–P(2)	2.513(3)
Re(2)–O(7)	2.176(7)
O(7)–C(7)	1.229(11)
Re(2)–O(7)–C(7)	131.1(7)
Au(1)–C(7)–O(7)	123.4(8)
P(3)–Au(1)–C(7)	178.6(3)

Chemicals. The solids $HPPh_2$ and $Re_2(CO)_{10}$ were purchased from Strem and Janssen. The RLi (R = Me, *n*-Bu, *t*-Bu, Ph) solutions were purchased from Fluka. $Re_2(\mu\text{-}PPh_2)_2(CO)_8$ was prepared according to literature methods [27].

3.1. Preparation of the lithium salts Li[$Re_2(\mu\text{-}PPh_2)(ax\text{-}C(R)O)(CO)_7$ (R = Me **1a**, n-Bu **1b**, t-Bu **1c**, Ph **1d**) and of the neutral heterometallic title compounds $Re_2(\mu\text{-}PPh_2)_2(CO)_7$ (ax-RCOAuPPh$_3$) (R = Me **2a**, n-Bu **2b**, t-Bu **2c**, Ph **2d**)

To $Re_2(\mu\text{-}PPh_2)_2(CO)_8$ (159 mg; 0.16 mmol) in THF (10 ml) at −90°C, an equimolar amount of the LiR (R = Me, *n*-Bu, *t*-Bu, Ph) solution was added. The solution was stirred at −90°C for 10 min and then warmed to room temperature. The formation of **1a–b** and **1d** was controlled by ^{31}P NMR and found to be quantitative. In the case of **1c**, the yield was somewhat diminished because of the known side-reaction between *t*-BuLi and THF. After removal of the solvent in vacuo, the yellow lithium salts remained as solids. Each of the lithium salts (0.16 mmol) obtained was reacted with an equimolar amount of $ClAuPPh_3$ (77 mg) in chloroform solution at room temperature for 30 min and each of the products were separated by PLC (plate, silica gel 60 F_{254}, Merck) using the following solvent mixture: **1a**, acetone-*n*-hexane = 1:3; **1b**, dichloromethane-*n*-hexane = 1:1; **1c**, acetone-*n*-hexane = 1.5:2; **1d**, acetone-*n*-hexane = 1:2.5. The yellow crystals of **1a–d** remained after evaporation of the solvent with following yields: **1a**, 78% (150 mg); **1b**, 75% (140 mg); **1c**, 24% (47 mg); **1d**, 61% (142 mg).

3.2. Spectroscopic data

δ values ^{1}H MR-spectra ($CDCl_3$, standard TMS): **1a**, 2.18 (s, 3H, CH_3), 7.0–7.12 (m, 4H, *p*-H(Ph)), 17–7.29 (m, 8H, *m*-H(Ph)), 7.61–7.77 (m, 8H, O–H(Ph)); **1b** 0.73 (t, 3H, CH_3, $^3J_{HH} = 7.1$ Hz), 0.86–0.94 (m, 2H, CH_2) 1.06 (m, 2H, CH_2), 2.72 (t, 2H, CH_2, $^3J_{HH} = 7.7$ Hz), 7.09–7.78 (m, 20H, Ph); **1c**, 0.94 (s, 9H, *t*-Bu), 7.02–7.72 (m, 20H, Ph).

δ values ^{31}P NMR-spectra (THF, standard 85% H_3PO_4): **1a** −137.3 (s, 2P, μ-P), −133.4 (CD_2Cl_2 solution); **1.6**, −137.9 (s, 2P, μ-P), −132.6 (CD_2Cl_2); **1a**, −129.6 (s, 2P, μ-P), −130.5 ($CDCl_3$); **1d**, −131.3 (s, 2P, μ-P).

IR data for υ(CO) absorption bands (cm^{-1}) in THF: **1a**, 2077 s, 1994 vs, 1969 sh, 1928 s, 1898 vs, 1884 vs, 1539 m; **1b**, 2079 s, 1992 s, 1973 sh, 1928 s, 1896 vs, 1882 vs, 1537 m; **1c**, 2077 s, 1994 s, 1973 sh, 1913 s, 1878 vs, 1865 s, 1538 w; **1d**, 2077 s, 1996 vs, 1977 sh, 1913 s, 1884 s, 1869 vs, 1946 w.

δ values ^{1}H NMR-spectra ($CDCl_3$, standard TMS): **2a**, 2.19 (s, 3H, CH_3), 7.19–7.80 (m, 35H, Ph); **2b**, 0.80 (t, 3H, CH_3, $^3J_{HH} = 7.3$ Hz), 1.12–1.19 (m, 2H, CH_2), 1.44–1.52 (m, 2H, CH_2); 2.82 (t, 2H, CH_3, $^3J_{HH} = 6.7$ Hz), 7.13–7.82 (m, 35H, Ph), **2c**, 0.57 (s, 9H, *t*-Bu), 7.11–7.71 (m, 35H, Ph), **2d**, 6.88–7.78 (m, 40H, Ph).

δ values ^{31}P NMR-spectra ($CDCl_3$, standard 85% H_3PO_4): **2a**, −134.9 (s, 2P, μ-P), 39.1. (s, 1P, Pph_3); **2b**, −134.8 (s, 2P, μ-P), 39.4 (s, 1P, PPh_3); **2c**, −136.2 (s, 2P, μ-P), 39.7 (s, 1P, PPh_3); **2d**, −137.4 (s, 2P, μ-P), 39.9 (s, 1P, PPh_3).

IR data for υ(CO) modes (cm^{-1}) in THF: **2a**, 2079 s, 2013 sh, 2001 vs, 1990 sh, 1934 s, 1903 sh, 1894 sh, 1549 m; **2b**, 2081 m, 2002 vs, 1986 vs, 1936 s, 1901 (broad) s, 1888 s, 1537 m; **2c**, 2079 s, 2004 vs, 1992 sh, 1934 s, 1901 sh, 1891 vs, 1540 m; **2d** 2079 s, 2015 sh, 2005 s, 1930 s, 1907 sh, 1888 vs, 1508 m.

Elementary analysis: **2a**, ($AuC_{51}H_{38}O_8P_3Re_2$, M_r = 1441.16), C, 42.56 (calc. 42.50); H, 2.70 (2.66); **2b** ($AuC_{54}H_{44}O_8P_3Re_2$, 1483.24), C, 43.80 (43.73); H, 3.08 (2.99); **2c**, ($AuC_{54}H_{44}O_8P_3Re_2$ 1483.24), C, 43.69 (43.73); H, 3.07 (2.99); **2d**, ($AuC_{56}H_{40}O_8P_3Re_2$ 1503.23), C, 44.79 (44.75); H, 2.72 (2.68).

3.3. X-ray data collection, structure solution and refinement

A yellow crystal, size $0.15 \times 0.22 \times 0.50$ mm^3, was used for data collection at $T = 293$ K. Lattice parameters were refined from 28 reflections $16 < 2\theta < 34°$. A number of 13,530 intensities were collected $4 < 2\theta < 15°$, $-15 < h < 15$, $-18 < k < 18$, $0 < l < 24$; three standard reflections were recorded every 400 and showed 8% decrease, intensities were corrected accordingly. Lp correction, empirical absorption correction via psi-scans, min/max transmission 0.476/0.732, after merging ($R_{int} = 0.037$) 13,125 unique intensities. The structure was solved by direct and conventional Fourier methods, full-matrix least-squares refinement based on F^2 and 650 parameters; all but H-atoms refined anisotropically; hydrogen atoms were refined at idealized positions with riding model. The program used for structure solution and refinement was SHELXL V5 [28]. Lists of atomic coordinates, anisotropic displacement parameters, hydrogen atom coordinates and complete bond lengths and angles are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD 407210.

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