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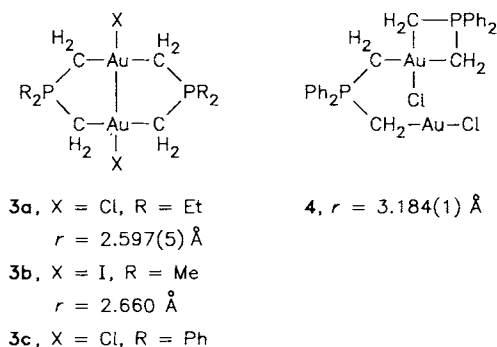
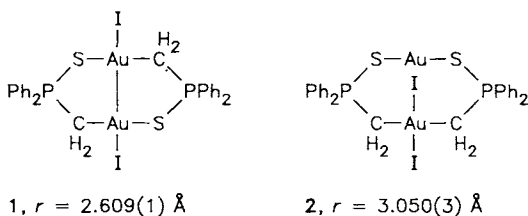
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- [16] **6b**: $^1\text{H-NMR}$ (CD_2Cl_2): $\delta = 1.5$ [dt, $^3J(\text{PH}) = 15$ Hz, CH_3], 2.1 (m, CH_2), 7.1–7.8 (m, C_6H_4). $^{31}\text{P-NMR}$ (CD_2Cl_2): $\delta = 34.6$ (s). MS (70 eV) $m/z = 726$ (calcd. 725).
- [17] **6d**: $^1\text{H-NMR}$ (CD_2Cl_2): $\delta = 1.65$ (s, CH_3), 7.1–7.8 (m, C_6H_4). MS (70 eV) $m/z = 756$ (calcd. 756).
- [18] **6b**: triclinic, $P1$, $a = 13.041(2)$, $b = 10.626(1)$, $c = 8.245(1)$ Å, $\alpha = 107.77(1)$, $\beta = 102.22(1)$, $\gamma = 90.90(1)^\circ$, $Z = 2$; Philips PW1100 diffractometer, $\lambda = 0.7107$ Å, $R = 0.032$, $R_w = 0.038$ for 3921 unique reflections [$4 < 2\theta < 55^\circ$, $I \geq 3\sigma(I)$], 431 parameters, H atoms by calculation, absolute configuration.
- [19] **6c**: triclinic, $P1$ [isomorphous with **6a** [13]], $a = 9.530(2)$, $b = 9.824(1)$, $c = 8.904(1)$ Å, $\alpha = 109.26(1)$, $\beta = 88.01(1)$, $\gamma = 103.96(1)^\circ$, $Z = 1$; PW1100 diffractometer, $\lambda = 0.7107$ Å, $R = 0.032$, $R_w = 0.022$ for 3937 unique reflections [$3 < 2\theta < 60^\circ$, $I \geq 3\sigma(I)$], 181 parameters, H atoms by calculation.
- [20] M. A. Bennett, S. K. Bhargava, K. D. Griffiths, G. B. Robertson, *Angew. Chem.* 99 (1987) 262; *Angew. Chem. Int. Ed. Engl.* 26 (1987) 260.
- [21] **10**: THF monoclinic, $P2_1/n$, $a = 15.459(1)$, $b = 13.668(2)$, $c = 10.970(1)$ Å, $\beta = 92.41(1)^\circ$, $Z = 4$; PW1100 diffractometer, $\lambda = 0.7107$ Å, $R = 0.032$, $R_w = 0.037$ for 2433 unique reflections [$3 < 2\theta < 50^\circ$, $I \geq 3\sigma(I)$], 253 parameters, H atoms by calculation.

Coupling of Cyclometalated Phenylphosphanes in Dinuclear Gold(II)-Complexes

By Martin A. Bennett,* Suresh K. Bhargava, K. David Griffiths, and Glen B. Robertson

Dinuclear complexes in which two gold(I) (5d^{10}) atoms are held in close proximity by a pair of bridging ligands^[1,2] undergo oxidative addition with halogens to give two types of product, in both of which the bridging framework is retained. For example, depending on the solvent, addition of iodine to the methylenethiophosphinate-gold(I) dimer $[\text{Au}_2\{\text{CH}_2\text{P}(\text{S})\text{Ph}_2\}_2]$ can yield either the isovalent gold(II)–gold(II)(d^9 – d^9) complex **1** or the isomeric, heterovalent gold(I)–gold(III)(d^{10} – d^8) complex **2**.^[3] Halogens add to the phosphorus ylide complexes $[\text{Au}_2\{(\text{CH}_2)_2\text{PR}_2\}_2]$, $\text{R} = \text{Me}$, Et, Ph, to form isovalent gold(II)–gold(II) complexes **3a**^[4]



Scheme 1. r = gold–gold distance.

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[*] X-ray structure analysis

and **3b**,^[5] but **3c** isomerizes in polar solvents to a heterovalent gold(I)–gold(III) dimer **4**, in which one of the ylide ligands is bound terminally to the gold(III) atom^[6] (see Scheme 1).

The cyclometalated dimer **5**^[7] reacts with bromine or iodine in a 1:1 molar ratio at -78°C to give orange-red crystalline complexes **6** and **7** in good yield.^[8] The fact that both show singlet $^{31}\text{P}\{^1\text{H}\}$ -NMR resonances^[9] suggests that the compounds have a symmetrical, isovalent structure and this is confirmed by an X-ray structural analysis of **7**^[10] (Fig. 1).^[11]

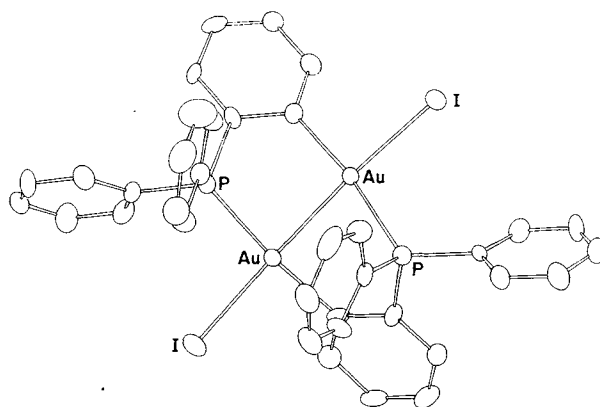
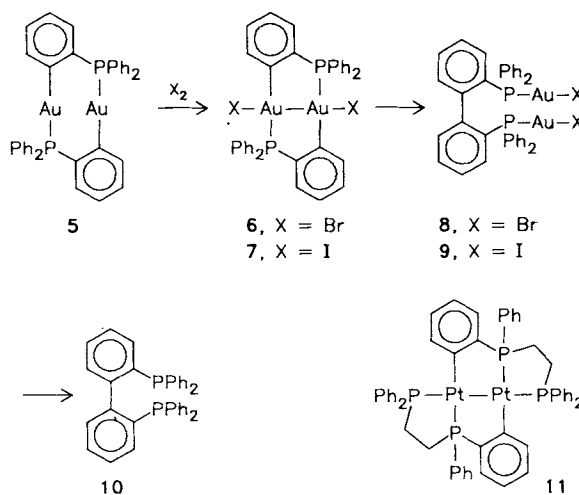


Fig. 1. Crystal structure of **7** [10, 11].

The Au–Au distances in **7** [2.5898(6) Å and 2.5960(7) Å for two independent molecules] are significantly shorter than the corresponding separation in its gold(I)–gold(I) precursor **5** [2.8594(3) Å].^[7] Moreover, whereas the metal-lacycle in **5** has a twist “recliner” conformation, that in **7** adopts a “propeller” conformation in order to reduce non-bonding interactions with the iodine atoms. The basic structure is very similar to that of the cyclometalated platinum(I)–platinum(I) (d^9 – d^9) complex **11**^[13] in which the axial ligands are phosphanes instead of iodine. The Au–Au distances in **7** are very close to those in the isovalent phosphorus ylide dichloro complex **3a**^[4] but are significantly less than those in the diiodo complex **3b**.^[5] The Au–I bond lengths in **7** [2.669 Å (av.)] are also significantly shorter than those in **3b** (2.699 Å).^[5]

When solutions of **6** and **7** are heated for ca. 12 h in toluene, or are allowed to stand in dichloromethane at room temperature for several days, the color changes from red to pale yellow; the same color change occurs more rap-



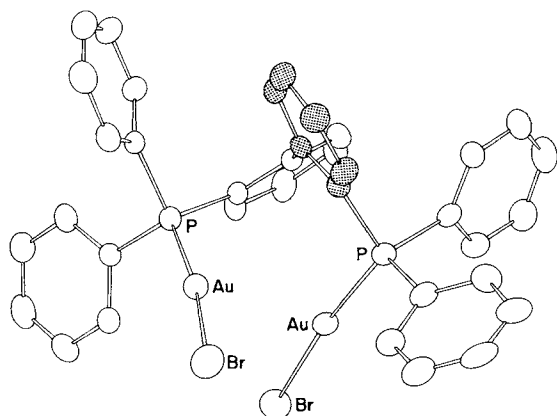


Fig. 2. Crystal structure of **8** [11, 16].

idly on exposure to normal laboratory light. Addition of hexane precipitates colorless, crystalline solids in yields of ca. 70%. The new complexes **8** and **9** are isomeric with their precursors, are dimeric in CH_2Cl_2 ,^[14] and show singlets in their $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra due to equivalent phosphorus atoms.^[15] X-ray analysis of the bromo-complex **8**^[16] (Fig. 2)^[11] shows that it contains a 2,2'-biphenylenebis(diphenylphosphane) ligand.^[17] A dihedral angle of 88.6° between the phenyl rings of the biphenyl unit leads to a separation of $3.3013(5)$ Å between the gold(I) atoms, which are not bound to each other and display their normal linear coordination. The Au-Br and Au-P bond lengths [av. 2.398 and 2.238 Å, respectively] are unexceptional.

Treatment of **9** with aqueous ethanolic NaCN liberates the ligand **10** quantitatively as a white, crystalline solid which melts at 212°C .^[18] The value is much higher than the m.p. of $68\text{--}70^\circ\text{C}$ reported for a product claimed to be **10** which was isolated in 65% yield from the reaction of Ph_2PCl with 2,2'-dilithiobiphenyl;^[19] unfortunately, no spectroscopic data for this compound were reported.

The isomerization of **6** to **8** and of **7** to **9** represents a reductive elimination of two σ -aryl groups at the digold(II) center. The reductive elimination of two σ -alkyl groups at a planar gold(III) center has been studied thoroughly,^[20] and the formation of biaryls from aryl-Grignard reagents or aryllithiums in the presence of transition metal halides is well known.^[21] The unusual feature in the present case is that the product of reductive elimination is held in the coordination sphere of the metal atoms by the phosphorus donors. This type of behavior has been observed previously only in the case of unsaturated ligands, e.g. in the conversion of the P,P' -ethylenebis(dicyclohexylphosphane) tetraphenylnickelacyclopentadiene complex into the corresponding η^4 -tetraphenylcyclobutadienenickel compound.^[22]

Although the mechanism of the process is as yet unknown, a plausible intermediate in the isomerization could be a heterovalent, salt-like gold(III)-gold(I) species $[\text{Au}^{\text{III}}(\text{o-C}_6\text{H}_4\text{PPh}_2)_2][\text{Au}^{\text{I}}\text{X}_2]$, $\text{X} = \text{Cl}, \text{Br}$. In the cation, the two σ -aryl groups would preferentially occupy *cis* coordination sites,^[23] thus favoring reductive elimination and formation of **8** and **9**.

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- [8] Procedure for **7**: A stirred suspension of **5** (300 mg, 0.33 mmol) in toluene (20 mL) contained in a Schlenk flask wrapped in aluminum foil was cooled to -60°C under nitrogen and treated dropwise with a solution of iodine (83 mg, 0.33 mmol) in toluene. The solution was allowed to warm to room temperature and was stirred for a further 1 h. The clear wine-red solution was concentrated in vacuo and hexane (15 mL) was added. On cooling to -10°C , a dark red crystalline solid separated within ca. 12 h. This was filtered in air and washed with hexane (3×5 mL) to give **7** (312 mg, ca. 80%), dec. $> 240^\circ\text{C}$. Complex **6** was obtained similarly from **5** and bromine. Satisfactory analytical data were obtained for this and other compounds described herein. Both **6** and **7** were found to be dimeric in CH_2Cl_2 by osmometry. **6**: M_r found, 967, calcd., 1076; **7**: found, 1145; calcd., 1170.
- [9] $^{31}\text{P}\{^1\text{H}\}$ -NMR (CD_2Cl_2 , external standard 85% H_3PO_4): $\delta = -4.6$ (**6**), $\delta = -13.2$ (**7**).
- [10] **7**· CH_2Cl_2 : triclinic, $A\bar{1}$, $a = 49.572(5)$, $b = 18.859(2)$, $c = 9.394(1)$ Å, $\alpha = 92.550(8)$, $\beta = 88.651(8)$, $\gamma = 54.453(6)^\circ$, $Z = 4$; FACS-1 diffractometer, $\lambda = 1.5418$ Å; $R = 0.033$, $R_w = 0.044$ for 6138 unique reflections [$3 < 2\theta < 100^\circ$, $I \geq 3\sigma(I)$], 784 parameters, H atoms by calculation.
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- [14] **9**: M_r (osmometric) 1194, calcd. 1169.
- [15] ^{31}P -NMR (CD_2Cl_2): $\delta = 28.0$ (**8**), 31.3 (**9**); the isomerizations **6** \rightarrow **8** and **7** \rightarrow **9** take place quantitatively, as shown by ^{31}P -NMR monitoring.
- [16] **8**: monoclinic, $P2_1/c$, $a = 10.897(2)$, $b = 16.183(3)$, $c = 18.890(4)$ Å, $\beta = 93.72(2)^\circ$, $Z = 4$; FACS-1 diffractometer, $\lambda = 0.7107$ Å; $R = 0.029$, $R_w = 0.031$ for 4082 unique reflections [$3 < 2\theta < 50^\circ$, $I \geq 3\sigma(I)$], 380 parameters, H atoms by calculation. Further details of the crystal structure investigations of **7** and **8** are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (UK).
- [17] The complex $[\text{Au}_2\text{Cl}_2(2,2'\text{-Et}_2\text{PC}_6\text{H}_4\text{C}_6\text{H}_4\text{PEt}_2)]$ has been mentioned briefly, without details: D. W. Allen, F. G. Mann, I. T. Millar, *J. Chem. Soc. C* 1967, 1869.
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- [23] The neutral platinum(II) complex $[\text{Pt}(\text{o-C}_6\text{H}_4\text{PPh}_2)_2]$, which is isoelectronic with the postulated gold(III) cation $[\text{Au}(\text{o-C}_6\text{H}_4\text{PPh}_2)_2]^+$, contains *cis*-aryl ligands: M. A. Bennett, S. K. Bhargava, G. B. Robertson, A. C. Willis, unpublished work.

Chemistry of Pyrrocorphins: Biomimetic Regioselectivity of C-Methylation at the Ligand Periphery of Magnesium(II) Uropyrrocorphinate(Type I)- octanitriles**

By Christian Leumann, Thomas Früh, Michael Göbel, and
Albert Eschenmoser*

Dedicated to Gerhard Quinkert on the occasion of his 60th birthday

As has recently been shown with octaethylporphyrinogen as a model system, the porphyrinogen \rightarrow pyrrocor-

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