JOM 23499

Substituted metal carbonyls

XXII *. Synthesis of 1,1′-bis(diphenylphosphino)ferrocene-bridged complexes with two heterometallic Au–M (M = Mn and Re) bonds

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(Received November 20, 1992; in revised form December 25, 1992)

Abstract

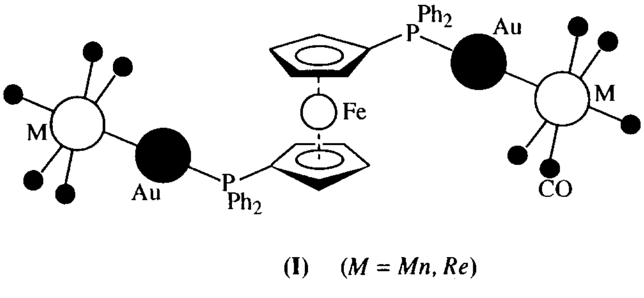
$Au_2Cl_2(\mu$-1,1′-bis(diphenylphosphino)ferrocene (dppf) reacts with $Na[M(CO)_5]$ to give $[AuM(CO)_5]_2(\mu$-dppf) (M = Re (**1**); M = Mn (**2**)) in 45% and 71% yields respectively. Both **1** and **2** represent pentametallic structures with a dppf metalloligand bridging between two heterometallic fragments which consist of Au–M bonds. The X-ray photoelectron spectroscopic data suggested polarization of the $Au^{\delta+}$–$Re^{\delta-}$ bonds in **1**. Contrary to **1**, $(CO)_9Re_2(\mu$-dppf)AuCl (**3**), which is synthesized from $Re_2(CO)_9$(dppf-*P*) and $AuCl(Me_2S)$ in 65% yield, shows binding energies typical of Au^I and Re^0. Reaction between $Au_2Cl_2(\mu$-dppf) and $K_2Pd(CN)_4$ resulted in no M–M bond but ligand displacement to give $Au_2(CN)_2(\mu$-dppf) (**4**) (yield, 8%) as the only isolable product.

1. Introduction

To date, many heterometallic complexes containing Au–M bonds have been reported. These include various bimetallic complexes (M = V [1], Mo [2], W [2], Mn [3], Re [4], Co [3a,5] Ir [6] and mixed-metal clusters [7]. These compounds are generally obtained via redox condensation between metal carbonyl anions and $AuCl(PR_3)$ [1–5,7a–7g], or via metal hydrido complexes and $AuCl(PR_3)$ or $AuMe(PPh_3)$ with concomitant elimination of HCl or methane [6,7h–7j]. With the recent isolation of $Au_2Cl_2(\mu$-P–P) (P–P = dppm, dppe, dppp), there opens up a possibility for the study of the cooperative effect of discrete Au–M cluster fragments via a diphosphine bridge. This approach has been recently represented in a synthesis of a multimetallic Au–Fe complex [8]. In this report, we extend this strategy to the synthesis of two novel complexes which contain Au–M (M = Mn, Re) bonds using $Au_2Cl_2(\mu$-dppf) (dppf-1,1′-bis(diphenylphosphino)ferrocene) as the substrate. Dppf is preferred as the bridging unit because of its high adaptability arising from its variable torsional twist [9]. The use of X-ray photoelectron spectroscopy (XPS) in the study of the Au–Re bond is also included. Although established as a surface technique, XPS has been widely applied as a probe to the chemical and electronic properties of various metal complexes [10]. Based on the proven correlation between metal binding energy (BE) and oxidation state [11], we could determine the extent of charge distribution across the heterometals upon M–M′ bond formation.

2. Results and discussion

$Na[M(CO)_5]$ reacts rapidly with $Au_2Cl_2(\mu$-dppf) to give a pentametallic complex $[AuM(CO)_5]_2(\mu$-dppf) (M = Re (**1**) and Mn (**2**)) comprising two heterometal bonds singly-bridged by a metallodiphosphine (**I**).



(**I**) (*M = Mn, Re*)

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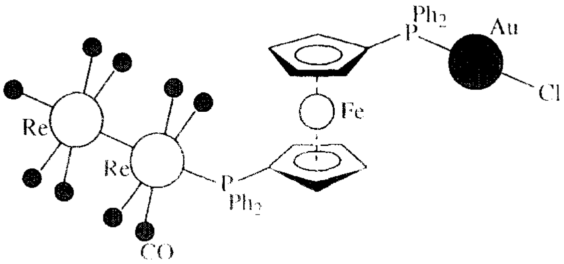
* For Part XXI see ref. 21(d).

Complex **1** is air and moisture stable in the solid state but **2** decomposes upon prolonged exposure to air. Their related complexes (Ph$_3$P)AuM(CO)$_5$ [3,4] which are isolobal [7g,12] to HM(CO)$_5$ [13] and M$_2$(CO)$_{10}$ have been reported. The isolobality analogy can be extended to the Au$_2$(μ-dppf) fragment and thus complexes **1** and **2** can be treated as isolobal to the hypothetical [HM(CO)$_5$]$_2$ and [M$_2$(CO)$_{10}$]$_2$ dimers. A dppf derivative of the latter can be found in [M$_2$(CO)$_9$]$_2$(μ-dppf) which has recently been characterized [14].

The carbonyl absorptions in the IR spectra are characteristic of a [M(CO)$_5$] moiety with a near-C_{4v} symmetry. Assignments of the IR-active modes follow those described for [(PhO)$_3$P]AuMn(CO)$_5$ [4]. The observed shoulder peaks (1997 cm^{-1} for **1** and 1995 cm^{-1} for **2**) arise from the B_1 vibration which is made IR active by the lowering of the molecular symmetry by the phosphino group. Both ^{1}H and ^{31}P NMR spectra conform to an open bridge of dppf symmetrically disposed between two heterometal units. The higher shielding of the ^{31}P resonance in **2** denotes the lower electronegativity (Pauling's scale) of Mn (1.55) compared with Re (1.90) [15] and hence a lower electron drift from Au to the metal carbonyl site in **2**.

Evans and Mingos [12] have calculated the relative energy of the frontier orbitals of the Au(PH$_3$) and Mn(CO)$_5$ fragments. The high-lying nature of the hy(s-z) orbital of the former compared with the latter suggests that, in (Ph$_3$P)AuMn(CO)$_5$ [3a] and its related complexes, the M–M′ bond formed will be polarized (Au$^{\delta+}$–Mn$^{\delta-}$) despite a zero formal oxidation state for both metal centres. The X-ray photoelectron spectra of **1** and Au$_2$Cl$_2$(μ-dppf) [16] were recorded and compared. On displacement of Cl by Re(CO)$_5$, both Au(4f$_{7/2}$) and P(2p) BEs decrease by 0.6 eV and 0.4 eV respectively. This indicates an increase in electron density on both Au and P sites, which is a direct consequence of a decrease in the formal oxidation state (OS) of Au from +1 in Au$_2$Cl$_2$(μ-dppf) to zero in **1**. Further comparison of the Re(4f$_{7/2}$) BE of **1** (41.9 eV) with those of Re$_2$(CO)$_{10}$ (42.4 eV) and ReBr(CO)$_5$ (43.0 eV) [14] pointed to the subzero effective OS of Re in **1**. A similar study of the Au(4f$_{7/2}$) BE of **1** (84.9 eV) compared with those of Au metal (84.0 eV) [17] and Au$_2$Cl$_2$(μ-dppf) (85.5 eV) [16] confirms that the OS of Au in **1** is intermediary between +1 and 0. The Au–Re bond in **1** is thus shown to be significantly polarized even though the net dipole of the complex is zero based on the molecular symmetry. A similar polarization effect of other heterometal bonds has been noted in other XPS studies [18]. In order to demonstrate further the M–M′ bonding effect on the charge distribution, we synthesized a similar complex (CO)$_9$Re$_2$(μ-dppf)AuCl (**3**) in which an Au$^{\text{I}}$ centre is attached to a Re(0) carbonyl moiety through a dppf bridge and without any direct Au···Re interaction (**II**).



(**II**)

The observed Au(4f$_{7/2}$) BE (85.4 eV) is essentially the same as that in Au$_2$Cl$_2$(μ-dppf) which suggests no charge influx across the dppf bridge in **3**. The broadness of the Re(4f) bands in **3** indicates some slight chemical inequivalence of the Re sites. Gaussian deconvolution gives rise to two Re(4f$_{7/2}$) values of 42.1 eV and 41.5 eV, both of which are indicative of Re^0. The lower energy band belongs to the phosphine substituted [Re(CO)$_4$] site and reflects the σ donor character of dppf.

The facility of the reaction between [M(CO)$_5$]$^-$ and Au$_2$Cl$_2$(μ-dppf) lies largely in the weakness of the Au–Cl bonds which in turn can be explained by the mismatch of soft Au(I) and hard Cl$^-$ [19]. In general, Au$_2$Cl$_2$(μ-dppf) provides easy access to dppf-bridged digold complexes. Whether heterometallic Au–M bonds are formed depends, however, on the incoming metallate. This is best exemplified in the reaction between Au$_2$Cl$_2$(μ-dppf) and [Pd(CN)$_4$]$^{2-}$. No Au–Pd bonded species is evident, and the only species isolated is characterized as a ligand-exchange product Au$_2$(CN)$_2$(μ-dppf) (**4**). Chloride migration is likely to have occurred via a cyano-bridged complex which is too unstable to be isolated.

3. Conclusion

Complexes **1** and **2** are the first examples which show the bridging of two heterodimetallic units by dppf. We have previously shown that dppf can bridge between two homomononuclear [20] and heteromononuclear [21] moieties, two homodimetallic functionalities [14], or a combination of mononuclear and dinuclear fragments [21b,c].

4. Experimental details

4.1. General comments

All reactions were performed under pure dry argon using standard Schlenk techniques. Au$_2$Cl$_2$(μ-dppf)

[22] was prepared by a modified procedure from AuCl(SMe$_2$) [23] and dppf [24] in a 2:1 molar ratio [16]. $K_2Pd(CN)_4$ [25] and Re$_2$(CO)$_9$(dppf-*P*) [14] were prepared by methods given in the literature. Na[M(CO)$_5$] (M = Mn, Re) were obtained by a sodium amalgam (3%) reduction of the binary metal carbonyls [26]. All other chemical reagents were commercial products and used as received. The procedures and instruments used were as described previously [20a,21a]. Fourier transform IR (FTIR) spectra were recorded with either a Perkin–Elmer 1710 or 1725X FTIR spectrometer. All NMR spectra were recorded in $CDCl_3$ solutions on a Bruker AC 300F spectrometer. The ^{31}P NMR chemical shifts are externally referenced to 85% H_3PO_4. Core level X-ray photoelectron spectra were obtained on a VG ESCA/SIMSLAB MKII spectrometer as published previously [14]. Values of the full width at half-maximum of the binding energies are given in parentheses. Deconvolution of the overlapping spectral components was performed using VG software. In the simulated spectra, each Re(4f) doublet was constrained to have a spin–orbit splitting of 2.4 ± 0.1 eV and a Re(4f$_{7/2}$):Re(4f$_{5/2}$) signal intensity ratio of 4:3. Silica TLC plates of 0.25 mm were obtained from Merck. Elemental analyses were performed by the analytical service of this department. The Au microanalytical data are unsatisfactory because of the matrix effect. The samples could not be digested in aqueous systems other than aqua regia. The analysis was carried out by ICP using 1000 μg cm^{-3} in 20% HCl as the standard. The presence of solvate molecules in the sample was confirmed by NMR analysis. The solvent inclusion in the crystal lattice of many dppf complexes has been noted in the literature (see for example ref. 27).

4.2. Synthesis of [AuRe(CO)$_5$]$_2$(μ-dppf) (1)

[Re(CO)$_5$]$^-$ generated *in situ* from Re$_2$(CO)$_{10}$ (0.065 g, 0.100 mmol) and Na–Hg (about 0.3 g) was cooled to 0°C and filtered dropwise into a continuously stirred solution of Au$_2$Cl$_2$(μ-dppf) (0.090 g, 0.088 mmol) in tetrahydrofuran (THF) (5 cm^3) at −78°C. The resultant chrome-yellow solution was stirred at −78°C for 5 min, after which it was slowly warmed to room temperature (RT). Stirring was continued for another 4 h to obtain a cloudy deep-orange solution. After removal of the solvent, the residue was washed with MeOH and recrystallized from a CH_2Cl_2–MeOH mixture to give orange crystals of [AuRe(CO)$_5$]$_2$(μ-dppf) (yield, 0.063 g (45%)).

(Found: C, 33.13; H, 1.58; P, 4.22; Fe, 3.24; Au, 22.07%. $C_{44}H_{28}Au_2FeO_{10}P_2Re_2$ requires: C, 33.01; H, 1.76; P, 3.87; Fe, 3.49; Au, 24.61%.) ν(CO): 2082m, 1997w(sh), 1970vs(br) cm^{-1} ($CHCl_3$). ^{1}H NMR: 7.50–7.37 (m, 20H, Ph); 4.81 (m, 4H, CpH$_\beta$); 4.18 (q, 4H, CpH$_\alpha$) ppm. ^{31}P NMR: 53.58 (s) ppm. XPS BE (FWHM): 131.8 (2.00) (P(2p)); 41.9 (1.80) (Re(4f$_{7/2}$)); 44.3 (1.80) (Re(4f$_{5/2}$)); 84.9 (1.95) (Au(4f$_{7/2}$)); 88.5 (1.95) (Au(4f$_{5/2}$)); 708.5 (1.80) (Fe(2p$_{3/2}$)) eV.

4.3. Synthesis of [AuMn(CO)$_5$]$_2$(μ-dppf) (2)

[Mn(CO)$_5$]$^-$ generated *in situ* from Mn$_2$(CO)$_{10}$ (0.055 g, 0.141 mmol) and Na–Hg (about 0.8 g) was cooled to 0°C and filtered dropwise into a continuously stirred solution of Au$_2$Cl$_2$(μ-dppf) (0.100 g, 0.099 mmol) in THF (8 cm^3) at 0°C. The reaction mixture was stirred at 0°C for 10 min followed by 2 h at RT to obtain a slightly cloudy orange solution. After removal of the solvent, the yellowish orange residue was extracted with CH_2Cl_2, precipitated from MeOH and recrystallized from a CH_2Cl_2–MeOH mixture to give orange crystals which were moderately air sensitive [AuMn(CO)$_5$]$_2$(μ-dppf) · 0.5CH_2Cl_2 (yield, 0.093 g (71%)).

(Found: C, 38.13; H, 2.08; P, 4.63; Fe, 4.17; Au, 24.20; Mn, 7.69%. $C_{44.5}H_{29}Au_2ClFeMn_2O_{10}P_2$ requires: C, 38.71; H, 2.12; P, 4.49; Fe, 4.04; Au, 28.53; Mn, 7.97%.) ν(CO): 2065m, 1995w(sh), 1955vs(br) cm^{-1} ($CHCl_3$). ^{1}H NMR: 7.54–7.32 (m, 20H, Ph); 5.30 (s, 1H, CH_2Cl_2); 4.80 (m, 4H, CpH$_\beta$); 4.19 (m, 4H, CpH$_\alpha$) ppm. ^{31}P NMR: 42.13 (s) ppm.

4.4. Synthesis of (CO)$_9$Re$_2$(μ-dppf)AuCl (3)

A solution of Re$_2$(CO)$_9$(dppf) (0.079 g, 0.067 mmol) in THF (15 cm^3) was transferred into a Schlenk flask containing solid AuCl(SMe$_2$) (0.029 g, 0.098 mmol) at RT. The resultant orange solution was shielded from direct light and stirred at RT for 1 h, after which four fifths of the solvent was removed *in vacuo*. Stirring was continued for 1 h, after which the solvent was removed and the residue extracted with CH_2Cl_2 and applied onto silica TLC plates. Elution with a mixture of CH_2Cl_2–hexane (7:13) moved one major orange band which, on extraction and recrystallization from CH_2Cl_2–MeOH yielded fine orange crystals of **3** (yield, 0.061 g (65%)) (melting point 183–184°C).

(Found: C, 36.89; H, 1.89; P, 4.71; Fe, 3.40; Au, 12.59; Cl, 2.60%. $C_{43}H_{28}AuClFeO_9P_2Re_2$ requires: C, 36.59; H, 2.00; P, 4.39; Fe, 3.96; Au, 13.96; Cl, 2.51%.) ν(CO): 2107m, 2030w, 1998vs, 1965m, 1936s cm^{-1} ($CHCl_3$). ^{1}H NMR: 7.49–7.34 (m, 20H, Ph); 4.72 (m, 2H, AuP–CpH$_\beta$); 4.41 (m, 2H, ReP–CpH$_\beta$); 4.22 (m, 2H, AuP–CpH$_\alpha$); 3.97 (m, 2H, ReP–CpH$_\alpha$) ppm. ^{31}P NMR: 28.27 (s, Au–P); 5.79 (s, Re–P) ppm. XPS BE (FWHM): 131.9 (2.05) (P(2p)); 41.5 (1.85) (Re(4f$_{7/2}$), P–Re); 42.1 (1.85) (Re($4f_{7/2}$), unsubstituted); 43.8 (1.85) (Re($4f_{5/2}$), P–Re); 44.4 (1.85) (Re($4f_{5/2}$), unsubstituted); 85.4 (2.05) (Au($4f_{7/2}$)); 89.0 (2.05) (Au($4f_{5/2}$)); 708.3 (1.55) (Fe($2p_{3/2}$)); 198.5 (1.85) (Cl($2p_{3/2}$)); 200.3 (1.85) (Cl($2p_{1/2}$)) eV.

4.5. Synthesis of $(AuCN)_2(\mu$-dppf) (4)

$K_2Pd(CN)_4$ (0.044 g, 0.15 mmol) in THF–H_2O (4:1) (10 cm^3) at 0°C was transferred into a stirred solution of $Au_2Cl_2(\mu$-dppf) (0.077 g, 0.075 mmol) in THF (7 cm^3) at 0°C. The resultant mixture was stirred for $\frac{1}{2}$h in an ice bath followed by 1 h at RT whereby an orange solution was obtained. After removal of the solvent *in vacuo*, the residue was extracted with CH_2Cl_2 and chromatographed on silica TLC plates (CH_2Cl_2 : hexane, 95 : 5). $(AuCN)_2(\mu$-dppf) was extracted from the main band by CH_2Cl_2 and recrystallized from CH_2Cl_2–hexane to give $[Au(CN)]_2(\mu$-dppf) (yield, 0.018 g (7.5%)).

(Found: C, 43.45; H, 2.69; N, 2.70; Au, 34.70; Fe, 6.43%. $C_{36}H_{28}Au_2ClFeN_2P_2$ requires: C, 43.22; H, 2.82; N, 2.80; Au, 39.38; Fe, 5.58%.) ν(CN): 2140 cm^{-1} (KBr). ^1H NMR: 7.53–7.44 (m, 20H, Ph); 4.69 (m, 4H, CpH_β); 4.27 (m, 4H, CpH_α) ppm. ^{31}P NMR: 34.60 (s) ppm.

Other products of this reaction are either too trace or too unstable to be isolated.

Acknowledgments

This work would not have been possible without the financial support from our University (RP 850030). Two of the authors (P.M.N.L. and Y.K.Y.) acknowledge the University for scholarship awards. The technical support from our department is appreciated.

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