Journal of Organometallic Chemistry, 391 (1990) C28–C32
Elsevier Sequoia S.A., Lausanne
JOM 20932PC

Preliminary communication

Synthesis and structural characterization of the first transition metal cluster containing a PPh_2AuPPh_3 ligand, $Ir_4(CO)_8(\mu\text{-}CO)_3(PPh_2AuPPh_3)$, and its conversion into $Ir_4(CO)_9(\mu\text{-}CO)(\mu\text{-}PPh_2)(\mu\text{-}AuPPh_3)$

Dario Braga *, **Fabrizia Grepioni**
Dipartimento di Chimica "G. Ciamician", Universita' degli Studi di Bologna, via F. Selmi 2, 40126 Bologna (Italy)

Fatima S. Livotto and Maria D. Vargas *
Instituto de Química, Universidade Estadual de Campinas, CP 6154 Campinas 13081, SP (Brazil)

(Received February 6th, 1990)

Abstract

Deprotonation of $Ir_4(CO)_{11}PPh_2H$ (1) in the presence of $[AuPPh_3][PF_6]$ yields the novel species $Ir_4(CO)_{11}(PPh_2AuPPh_3)$ (2), which possesses a tetrahedral framework bearing a terminally bound PPh_2AuPPh_3 ligand. When heated in toluene, 2 is converted into the phosphido species $Ir_4(CO)_{10}(\mu\text{-}PPh_2)(\mu\text{-}AuPPh_3)$.

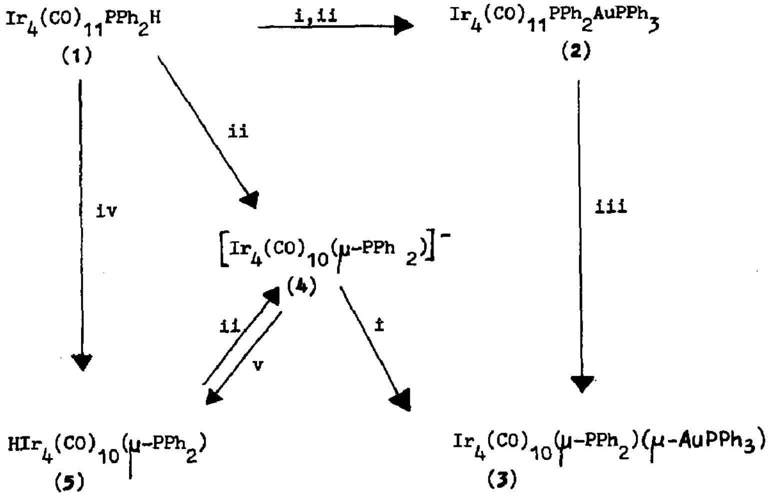
The synthesis and structural characterization of heteronuclear carbonyl clusters containing the $AuPR_3$ (R = alkyl, aryl) fragment linked to the metal core have been extensively investigated [1]. The main force behind the development of this area is the recognition that since this fragment and hydrogen are isolobal, they can often separately occupy the same coordination site when bound to transition metal clusters [2]. There are, however, only a few examples of $H/AuPPh_3$ replacement without structural change in main group elements or main-group-containing ligands linked to metal carbonyl clusters, e.g. $HFe_4(CO)_{12}CH/HFe_4(CO)_{12}CAuPPh_3$ [3], and there have been no comparative studies of the properties of such analogous species. We report here the synthesis of $Ir_4(CO)_{11}(PPh_2AuPPh_3)$ from $Ir_4(CO)_{11}(PPh_2H)$, which represents the first example of a $H/AuPPh_3$ replacement at the phosphorus of a coordinated secondary phosphine. We have also found that both species are converted into the corresponding phosphido-bridged complexes, viz. $Ir_4(CO)_{10}(\mu\text{-}PPh_2)(\mu\text{-}AuPPh_3)$ and $(\mu\text{-}H)Ir_4(CO)_{10}(\mu\text{-}PPh_2)$.

Addition of a CH_2Cl_2 solution of $Ir_4(CO)_{11}(PPh_2H)$ (1) [4] to a suspension of $AuPPh_3I$ and $TlPF_6$ that had been stirred for 1 h, followed by deprotonation in situ

0022-328X/90/\$03.50

with 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) affords [ca. in 90% yield after TLC (1 : 1 CH_2Cl_2–hexane)] a bright yellow crystalline compound, which is formulated as $Ir_4(CO)_{11}(PPh_2AuPPh_3)$ (**2**) on the basis of its spectroscopic data *. The outcome of this reaction depends critically on the order of addition of the reagents. Thus deprotonation of **1** in the absence of $AuPPh_3^+$, even in a CO-saturated solution, yields $[Ir_4(CO)_{10}(\mu\text{-}PPh_2)]^-$ (**4**), which can then be treated with $AuPPh_3^+$ to give $Ir_4(CO)_{10}(\mu\text{-}PPh_2)(\mu\text{-}AuPPh_3)$ (**3**) * in quantitative yield (see Scheme 1).

Complexes **1** and **2** exhibit similar behaviour when heated in toluene (10^{-4} *M*, 0.5 h, 100 °C and 80 °C, respectively). Carbonyl loss and quantitative conversion into **5** or **3**, respectively, are observed. Bright red crystals of **3** where obtained from CH_2Cl_2/hexane at room temperature.



Scheme 1. Reagents and conditions: i, $AuPPh_3I$, $TlPF_6$, CH_2Cl_2; ii DBU, CH_2Cl_2, iii toluene, 80 °C; iv toluene, 100 °C; v HBF_4, CH_2Cl_2.

---

* Spectroscopic data: **2**: ν_{CO}(hexane): 2082 m, 2052 vs, 2045 vs, 2015 m, 2003 m, 1998 msh, 1988 wsh, 1967 vwsh, 1880 vwsh, 1848 m, 1832 w, 1813 m cm^{-1}; $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 42.6 (d, PPh_3), 20.8 (d, PPh_2) [J_{P-P} 287.5 Hz, H_3PO_4 standard; **3**; ν_{CO}(hexane): 2070 s, 2042 vs, 2028 vs, 2015 vs, 1995 ssh, 2008 msh, 1996 wsh, 1845 wbd cm^{-1}; $^{31}P\{^1H\}$ NMR(CD_2Cl_2): δ 229.7 (d, PPh_2), 67.9 (d, PPh_3) [J_{P-P} 5.0 Hz]; NMR instrument: 400 MHz; fast atom bombardment MS with *p*-nitrobenzyl alcohol as matrix [calc ^{193}Ir, 1697 $[MH]^+$].

** Crystal data for **2**: $C_{41}H_{25}AuIr_4O_{11}P_2$, monoclinic, space group $P2_1/n$, *a* 9.336(6), *b* 16.308(4), *c* 28.862(7) Å, $\beta = 93.06(3)°$, *U* 4387.8 $Å^3$, $Z = 4$, *F*(000) 3103, $\mu(Mo\text{-}K_\alpha) = 149.7\ cm^{-1}$, θ-range 2.0–20 °, final *R* value 0.028 ($R_w = 0.027$) for 2130 of 4372 independent reflections [$I_0 < 2\sigma(I_0)$]; for **3**: $C_{40}H_{25}AuIr_4O_{10}P_2$, monoclinic, space group $P2_1/n$, *a* 11.836(5), *b* 27.581(5), *c* 14.532(2) Å, $\beta = 113.27(2)°$, *U* 4358.0 $Å^3$, $Z = 4$, $F(000) = 3048$, $\mu(Mo\text{-}K_\alpha) = 150.7\ cm^{-1}$, θ-range 2.0–25 °, final *R* value 0.052 ($R_w = 0.046$) for 2576 of 8145 independent reflections [$I_0 > 2\sigma(I_0)$]. Common to both data sets: diffraction intensities were collected at room-temperature by the $\omega - 2\theta$ scan method on an Enraf-Nonius CAD4 diffractometer. Fast decay under X-ray exposure and poor diffraction of the crystal prevented extension of the data collection of **2** beyond $2\theta = 40°$. Absorption correction was applied by the Walker and Stuart method [8]. Ir and P atoms in both **2** and **3**, and C and O atoms in **2**, were treated anisotropically. The H-atoms of the phenyl groups were placed in calculated positions (C–H 1.08 Å) and refined riding on their respective C-atoms. The phenyl groups were constrained to ideal geometry (C–C–C 120 °, C–C 1.395 Å). The SHELX76 package of programs [9] was used for all calculations.

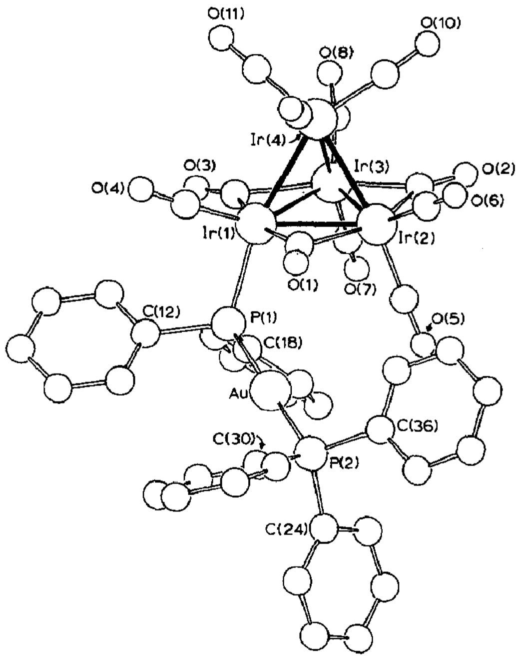


Fig. 1. The molecular structure of $Ir_4(CO)_{11}(PPh_2AuPPh_3)$. The C-atoms of the CO groups bear the same numbering as the corresponding O-atoms. H-atoms are omitted for clarity. Relevant bond distances (Å) and angles (°) are: Ir(1)–Ir(2) 2.732(1), Ir(2)–Ir(3) 2.706(1), Ir(3)–Ir(4) 2.701(1), Ir(1)–Ir(3) 2.745(1), Ir(2)–Ir(4) 2.713(1), Ir(1)–Ir(4) 2.722(1), Ir(1)–P(1) 2.36(1), Au–P(1) 2.34(1), Au–P(2) 2.30(1), Ir(1)–P(1)–Au 113.4(2), P(1)–Au–P(2) 177.9(2).

The crystal structures of **2** and **3** were established by an X-ray diffraction study **, and the molecules are shown in Figs. 1 and 2, respectively. Relevant bond distances and angles are listed in the captions. Both species possess a tetrahedral

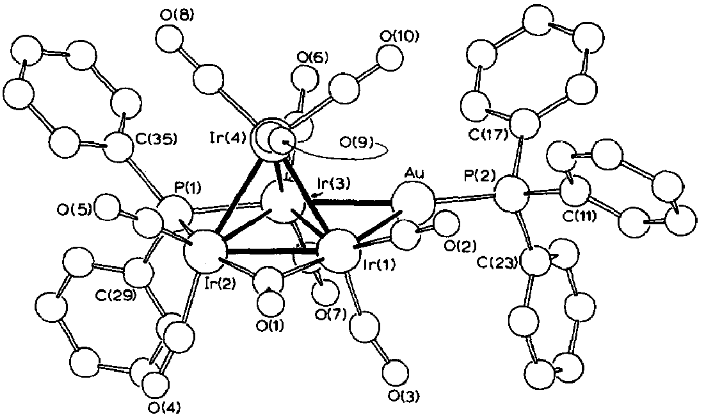


Fig. 2. The molecular structure of $Ir_4(CO)_{10}(\mu\text{-}PPh_2)(\mu\text{-}AuPPh_3)$. The C-atoms of the CO-groups bear the same numbering as the corresponding O-atoms. H-atoms are omitted for clarity. Relevant bond distances (Å) and angles (°) include: Ir(1)–Ir(2) 2.778(2) Ir(1)–Ir(3), 2.736(2), Ir(2)–Ir(3) 2.832(2), Ir(1)–Ir(4) 2.689(2), Ir(2)–Ir(4) 2.739(2), Ir(3)–Ir(4) 2.719(2), Ir(1)–Au 2.788(2), Ir(3)–Au 2.731(2), Ir(2)–P(1) 2.36(2), Ir(3)–P(1) 2.29(1), Au–P(2) 2.27(1), Ir(1)–Au–Ir(3) 59.4(1) Ir(2)–P(1)–Ir(3) 75.2(3).

Ir-framework with Ir–Ir bond lengths ranging from 2.701(1) to 2.745(1) Å in **2** [mean 2.720(1) Å] and from 2.689(2) to 2.832(2) Å in **3** [mean 2.749(2) Å]. In **2** one basal CO-ligand is formally replaced by the PPh_2AuPPh_3 unit which is attached to the cluster through the P of the PPh_2 group. The P–Au–P axis is linear [177.9(2)°], as it is in $[Au(PR_3)_2]^+$, from which **2** is formally derived by introduction of the $[Ir_4(CO)_{11}]^-$ fragment in place of a phenyl group. The Ir–P distance [2.36(1) Å] is comparable with those in many mono- and di-substituted Ir_4-species [5], implying that the ligand acts as a "normal" monodentate phosphine. As expected [6], the CO-bridged Ir–Ir basal bonds [mean 2.728(1) Å] are larger than the unbridged ones [mean 2.712(1) Å].

Far more interesting is the behaviour of **2** when heated. Loss of a CO ligand and oxidative addition of the coordinated PPh_2AuPPh_3 group results in a substantial ligand redistribution over the metal framework with cleavage of the PPh_2–$AuPPh_3$ bond. As shown from Fig. 2, the cluster base in **3** is now bridged by the $AuPPh_3$ and PPh_2 groups. This ligand arrangement is similar to that in **5** [7], providing a nice additional example of the isolobal analogy between the H and $AuPPh_3$ ligands. In both **2** and **3** the phosphido bridged bond is the longest [2.832(2) and 2.796(2) Å, respectively], while the Au-bridged bond in **3** appears to be shorter than the H-bridged one in **5** [2.736(2) compared will 2.769(2) Å] [7].

It should be emphasized that the similarity in the behaviour of the PPh_2H and PPh_2AuPPh_3 ligands in **1** and **2** suggests that the isolobal analogy between the H and $AuPPh_3$ ligands may also be of value in predicting the reactions of a given monohydrido or mono-$AuPPh_3$-containing cluster, simply on the basis of the behaviour of its analogues.

Care should be taken in extrapolating these ideas to compounds containing more than one $AuPR_3{}^+$ fragment, for which Au–Au interactions are common, whereas H–H interactions in the corresponding hydrido derivatives are unusual [1h,10]. We are currently studying the kinetics of the thermolysis of **1** and **2** and comparing the reactivities of **3** and **5**.

Acknowledgements. We thank S. Naylor for the FAB mass spectral measurements, the University Chemical Laboratory (Cambridge) for the ^{31}P NMR spectra, the CNP_q and FAPESP for research grants (MDV and FSL), and the Ministero Pubblica Istruzione (Italy) for financial support (DB and FG).

References

1 (a) P. Braunstein and J. Rose, Gold Bull., 18 (1985) 1 and references therein; (b) C.E. Housecroft and A.L. Rheingold, Organometallics, 6 (1987) 1332; (c) M.L. Blohm and W.L. Gladfelter, Inorg. Chem., 26 (1987) 459; (d) M.J. Freeman, A. G. Orpen and I.D. Salter, J. Chem. Soc., Dalton Trans., (1987) 379; (e) S.R. Drake, B.F.G. Johnson and J. Lewis, J. Organomet. Chem., 340 (1988) C31. (f) I.D. Salter, Adv. Organometal. Chem., 29 (1989) 249; (g) C.P. Horwitz, E.M. Holt, C.P. Brock and D.F. Shriver, J. Am. Chem. Soc., 107 (1985) 8136; (h) C.P. Horwitz and D.F. Shriver, J. Am. Chem. Soc., 107 (1985) 8147; (i) C.E. Hausecroft, M.S. Shongwe and A.L. Rheingold, Organometallics, 8 (1989) 2651; (j) A.M. Mueting, W. Bos, B.D. Alexander, P.D. Boyle, J.A. Casalnuovo, S. Balaban, L.N. Ito, S.M. Johnson and L.H. Pignolet, New J. Chem., 12 (1988) 505.

2 (a) J.W. Lauher and K.J. Wald, J. Am. Chem. Soc., 103 (1981) 7648; (b) K.P. Hall and D.M.P. Mingos, Prog. Inorg. Chem., 32 (1984) 237 and references therein.

3 (a) M.A. Beno, J.M. Williams, M. Tachikawa and E.L. Muetterties, J. Am. Chem. Soc., 120 (1980) 4542; (b) B.F.G. Johnson, D.A. Kaner, J. Lewis, P.R. Raithby and M.J. Rosales, J. Organomet. Chem., 231 (1982) C59.

4 J.N. Nicholls, P.R. Raithby and M.D. Vargas, J. Chem. Soc., Chem. Commun., (1986) 1617.

5 (a) R. Ros, A. Scrivanti, V.G. Albano, D. Braga and L. Garlaschelli, J. Chem. Soc., Dalton Trans., (1986) 2411; (b) J.R. Shapley, G.F. Stuntz, M.R. Churchill and J.P. Hutchinson, J. Am. Chem. Soc., 101 (1979) 7425.

6 D. Braga and F. Grepioni, J. Organomet. Chem., 336 (1987) C9.

7 P.R. Raithby and M.D. Vargas, 3rd Platinum Metals Conference, Sheffield, U.K., 1987, full manuscript in preparation

8 N. Walker and D. Stuart, Acta Crystallogr., A39 (1983) 158.

9 G.M. Sheldrick, SHELX76 package of computer programs, University of Cambridge, 1976.

10 T.P. Fehlner, C.E. Housecroft, W.R. Scheidt and K.S. Wong, Organometallics, 2 (1983) 825.