Inorganica Chimica Acta, 104 (1985) L29–L30

Organometallic Compounds of Iridium and Rhodium. XXVII*. $(t\text{-}Bu_2PCH_2CMe_3)IrH(Cl)(CH_2CMe_2CH_2P\text{-}Bu_2\text{-}t)$: A Metallacyclic Iridium Complex Formed by Metal Atom Insertion into a Neopentyl C–H Bond

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Received May 2, 1985

In a recent communication [1], we have described the binuclear cyclometallated hydrido iridium(III) complexes $(C_8H_{14})_2Ir\text{–}\mu\text{-}Cl_2\text{–}IrH[CH_2CMe_2CH_2P(CH_2CMe_3)_2][P(CH_2CMe_3)_3]$, $[t\text{-}BuP(CH_2CMe_3)_2]_2H_2Ir\text{–}\mu\text{-}Cl_2\text{–}IrH[CH_2CMe_2CH_2P(Bu\text{-}t)CH_2CMe_3]\cdot[t\text{-}BuP(CH_2CMe_3)_2]$, and $(t\text{-}Bu_2PCH_2CMe_2CH_2)HIr\text{–}\mu\text{-}Cl_2\text{–}IrH(CH_2CMe_2CH_2PBu_2\text{-}t)$ obtained from $Ir_2Cl_2(C_8H_{14})_4$ and the phosphines $t\text{-}Bu_{3-n}P(CH_2CMe_3)_n$ (n = 3, 2, 1) in hot toluene. Treatment of the labile cyclooctene iridium(I) precursor with di-t-butyl(neopentyl)phosphine also gave the dihydride $IrH_2(Cl)(t\text{-}Bu_2PCH_2CMe_3)_2$ [1] and, as we now know, a mononuclear species of composition '$IrCl(t\text{-}Bu_2PCH_2CMe_3)_2$'. This complex separated from the toluene/hexane mother liquors of $Ir_2Cl_2(C_8H_{14})_4$/$t\text{-}Bu_2PCH_2CMe_3$ reaction mixtures as slowly growing orange crystals. Solutions in C_6D_6 of the crystals thus obtained showed a ^1H NMR hydride triplet at δ −32.83, $^2J(PH)$ = 14.2 Hz, and a ^{31}P NMR AB pattern characterized by $\delta(P_A)$ = 70.3 ppm, $\delta(P_B)$ = 44.7 ppm, and $^2J(P_AP_B)$ = 347 Hz. These data are consistent [2–5] with a metallacyclic hydrido iridium(III) complex $(t\text{-}Bu_2PCH_2CMe_3)IrH(Cl)(CH_2CMe_2CH_2P\text{-}Bu_2\text{-}t)$ (**1**), the overall molecular geometry of which should correspond to distorted trigonal-bipyramidal [6, 7] with the phosphine ligands occupying *trans* positions [1, 3, 4]. The X-ray structural analysis, described hereafter, clearly established the *trans*-$(t\text{-}Bu_2PCH_2CMe_3)\text{–}IrCl\text{–}(CH_2CMe_2CH_2PBu_2\text{-}t)$ moiety of **1**.

X-ray measurements were made at room temperature on a Syntex $P2_1$ instrument using MoKα radiation (λ = 71.069 pm). The data were obtained from one of several specimens examined, each of which revealed a minor unseparable twin component. The notorious presence of these small twin components in the crystals of **1** resulted in diffraction intensities of poor quality and thus gave rise to unusually high residuals (*vide infra*).

Crystals of **1**, $C_{26}H_{58}ClIrP_2$ (660.4), were found to be triclinic, space group $P\bar{1}$, with a = 881.6(5), b = 913.6(6), c = 2122(2) pm, α = 90.24(6), β = 98.09(6), γ = 115.13(5)°, V = 1528 × 10^6 pm^3, Z = 2, *and* D_c = 1.44 g cm^{-3}. A total of 3749 unique intensities with 5° ⩽ 2θ ⩽ 44° was collected in the ω scan mode. Of these, 2515 gave counts with $I > 2.5\sigma(I)$ and were used in the structure determination. The intensity data were corrected for Lorentz, polarization, and absorption effects (μ = 43.9 cm^{-1}). The structure was solved by the heavy-atom method and refined by a full-matrix least-squares procedure with allowance for anisotropic thermal behaviour of the Ir, Cl, and P atoms, and isotropic vibrations of the carbon atoms. Hydrogen atoms were not included. With unit weights, refinement converged at R = 0.113 and R_w = 0.128. All computations were performed with the SHELX 76 program package. Final atomic positions are presented in Table I. Relevant bond distances and angles are given in the caption to Fig. 1 showing the molecular arrangement and the numbering scheme of the non-hydrogen atoms of the complex.†

The metal–phosphorus distance within the unmetallated $Ir\text{-}P(Bu\text{-}t)_2CH_2CMe_3$ fragment, 240.2(9) pm, is longer than those of 232.6(4) and 233.9(4)

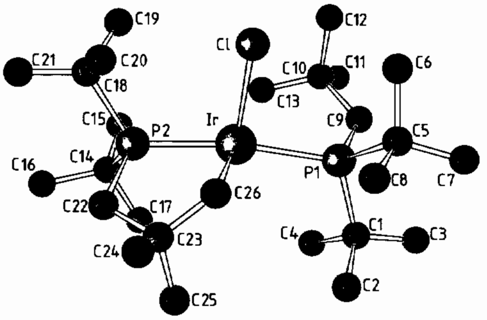

Fig. 1. Molecular arrangement and numbering scheme of the non-hydrogen atoms of **1**. Selected bond lengths (pm) and angles (°) are: P1–Ir, 240.2(9); P2–Ir, 233.6(9); Cl–Ir, 251.3(9); C26–Ir, 217(2). P2–Ir–P1, 167.8(3). Cl–Ir–P1, 93.1(3); Cl–Ir–P2, 98.7(3); C26–Ir–P1, 102.8(5); C26–Ir–P2, 80.2(5); C26–Ir–Cl, 91.2(5).

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*For Part XXVI, see ref. 1.

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*Further crystallographic information including tables of thermal parameters and F_o/F_c listings is available from the Fachinformationszentrum Energie, Physik, Mathematik GmbH (in cooperation with the Cambridge Crystallographic Data Centre), D-7514 Eggenstein-Leopoldshafen 2 (F.R.G.). Any request should be accompanied by the registration number CSD-51360, as well as by the full literature citation for this communication.

0020-1693/85/$3.30

TABLE I. Atomic Coordinates.

Atom	*x/a*	*y/b*	*z/c*
Ir	0.1125(2)	0.3291(2)	0.2421(1)
P(1)	0.2793(10)	0.4949(9)	0.3371(5)
P(2)	−0.0809(10)	0.2022(10)	0.1497(4)
Cl	0.2225(11)	0.1187(10)	0.2640(5)
C(1)	0.290(2)	0.712(2)	0.340(1)
C(2)	0.389(2)	0.813(2)	0.288(1)
C(3)	0.370(2)	0.805(2)	0.406(1)
C(4)	0.104(2)	0.689(2)	0.322(1)
C(5)	0.511(2)	0.513(2)	0.357(1)
C(6)	0.505(2)	0.344(2)	0.374(1)
C(7)	0.618(2)	0.635(2)	0.414(1)
C(8)	0.592(2)	0.568(2)	0.295(1)
C(9)	0.165(2)	0.417(2)	0.409(1)
C(10)	0.013(2)	0.249(1)	0.403(1)
C(11)	−0.080(2)	0.267(2)	0.457(1)
C(12)	0.071(2)	0.109(2)	0.416(1)
C(13)	−0.105(2)	0.207(2)	0.341(1)
C(14)	−0.294(2)	0.223(2)	0.143(1)
C(15)	−0.404(2)	0.109(2)	0.188(1)
C(16)	−0.392(2)	0.179(2)	0.072(1)
C(17)	−0.256(2)	0.399(2)	0.162(1)
C(18)	−0.118(2)	−0.017(2)	0.121(1)
C(19)	−0.177(2)	−0.118(2)	0.183(1)
C(20)	0.055(2)	−0.006(2)	0.113(1)
C(21)	−0.249(2)	−0.099(2)	0.062(1)
C(22)	0.024(2)	0.325(2)	0.083(1)
C(23)	0.198(2)	0.463(2)	0.108(1)
C(24)	0.323(2)	0.471(2)	0.061(1)
C(25)	0.192(2)	0.629(2)	0.111(1)
C(26)	0.276(2)	0.427(2)	0.171(1)

pm which were observed for the related dihydride $IrH_2(Cl)(t\text{-}Bu_2PCH_2CMe_3)_2$ [1]. In this latter complex, the *trans* P–Ir–P angle amounts to 167.3(1)° [1]. The P–Ir–P unit of **1** is characterized by a bond angle of 167.8(3)° and thus deviates from linearity in a similar way. The Ir–P bond length of 233.6(9) pm found for the metallacycle may be compared with those of 229.9(3)–231.5(3) pm exhibited by the bicyclic systems $IrH(Cl)[t\text{-}Bu\text{-}PCH_2CH(R)\text{-}CHCH_2CH_2PBu\text{-}t_2]$ (R = H, Me) [2, 3]. The endocyclic P–Ir–C angle of 80.2(5)° observed for **1** is close to the 82.8° characterizing the chelates of the dimeric platinum complex $[t\text{-}Bu_2PCH_2CMe_2CH_2\text{-}PtCl]_2$ [8]. In both this platinum(II) derivative and the metallacyclic hydrido iridium(III) compound, reported herein, the five-membered rings adopt an envelope conformation. The structure of **1** also demonstrates the aspect of M•••C–H proximity which is known to facilitate the formation of metallated rings in transition metal complexes containing bulky phosphine ligands [9]: the distance between the central metal and the methyl carbon C(13) measures *ca.* 293 pm which is 50–60 pm less than the typical van der Waals contact between a carbon and a platinum metal atom!

Acknowledgements

We gratefully acknowledge financial support by the Fonds der Chemischen Industrie. Thanks are also expressed to Degussa, Hanau, for a generous gift of iridium salts.

References

1 L. Dahlenburg and A. Yardimcioglu, *J. Organomet. Chem.*, in press.
2 C. Croccker, H. D. Empsall, R. J. Errington, E. M. Hyde, W. S. McDonald, R. Markham, M. C. Norton, B. L. Shaw and B. Weeks, *J. Chem. Soc., Dalton Trans.*, 1217 (1982).
3 R. J. Errington, W. S. McDonald and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1829 (1982).
4 W. J. Youngs and J. A. Ibers, *J. Am. Chem. Soc., 105,* 639 (1983).
5 P. E. Garrou, *Chem. Rev., 81,* 229 (1981).
6 H. D. Empsall, E. M. Hyde, E. Mentzer, B. L. Shaw and M. F. Uttley, *J. Chem. Soc., Dalton Trans.*, 2069 (1976).
7 S. Hietkamp, D. J. Stufkens and K. Vrieze, *J. Organomet. Chem., 152,* 347 (1978).
8 R. Mason, M. Textor, N. Al-Salem and B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, 292 (1976).
9 B. L. Shaw, *J. Am. Chem. Soc., 97,* 3856 (1975); *J. Organomet. Chem., 200,* 307 (1980).