is underway.

Acknowledgment. Thanks are due to Dr. Jean-Claude Daran for the X-ray structure determination and for helpful discussions.

Supplementary Material Available: Tables of positional and anisotropic thermal parameters, bond distances and angles, and least-squares planes (6 pages); a table of structure factors (9 pages). Ordering information is given on any current masthead page.

Phase-Transfer-Catalyzed Cleavage of Carbon–Hydrogen and Carbon–Phosphorus Bonds in PPh_3 by an Iridium Complex. Synthesis and Molecular Structure of $[Ir_2(C_5Me_5)_2(\mu\text{-}H)(\mu\text{-}PPh_2)(\mu\text{-}C_6H_4)]$

Vladimir V. Grushin,*[†] Alexei B. Vymenits, Alexander I. Yanovsky, Yuri T. Struchkov, and Mark E. Vol'pin

Institute of Organo-Element Compounds of the USSR Academy of Sciences, Moscow, USSR

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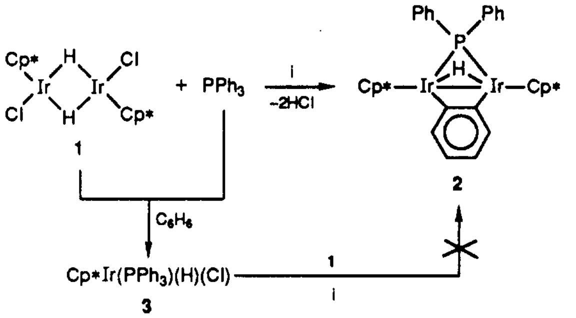
Summary: Reaction of $[(C_5Me_5IrCl)_2(\mu\text{-}H)_2]$ (**1**) with PPh_3 in benzene/60% aqueous $KOH/[PhCH_2NEt_3]^+Cl^-$ leads to the elimination of 2 equiv of HCl from **1**, oxidative addition of C–P and C–H bonds to iridium, and formation of the dinuclear complex $[Ir_2(C_5Me_5)_2(\mu\text{-}H)(\mu\text{-}PPh_2)(\mu\text{-}C_6H_4)]$ (**2**); the X-ray structure of **2** showed that it has bridging hydrido, diphenylphosphido, and *o*-phenylene ligands.

Phase-transfer catalysis (PTC) can be effectively used for the α-elimination of HCl from mononuclear chloro hydrido complexes of platinum,[1] iridium,[2,3] ruthenium,[3,4] and rhodium[3,4] and for the generation of reactive, coordinatively unsaturated complexes or their synthons. Here, we report the first and novel example of HCl elimination from a dinuclear chloro hydrido transition-metal complex under PTC conditions.

The reaction of $[\{(C_5Me_5)IrCl\}_2(\mu\text{-}H)_2]$ (1)[5] with PPh_3 in benzene/60% aqueous KOH, with $[PhCH_2NEt_3]^+Cl^-$ as the phase-transfer catalyst, resulted in the elimination of two molecules of HCl from 1 and formation of the new complex $[Ir_2(C_5Me_5)_2(\mu\text{-}H)(\mu\text{-}PPh_2)(\mu\text{-}C_6H_4)]$ (2; yield 50–60%, based on ^1H NMR spectroscopy) with bridging hydrido, diphenylphosphido, and *o*-phenylene ligands.[6] ^1H NMR spectroscopy[7] revealed that the reaction mixture contains another complex (3; ca. 30%), which is thought to arise from a known homogeneous reaction between 1 and PPh_3[5] (Scheme I).

Scheme I[a]



[a] $Cp^* = \eta^5\text{-}C_5Me_5$. The letter i denotes PhH/60% aqueous $KOH/[PhCH_2NEt_3]^+Cl^-$.

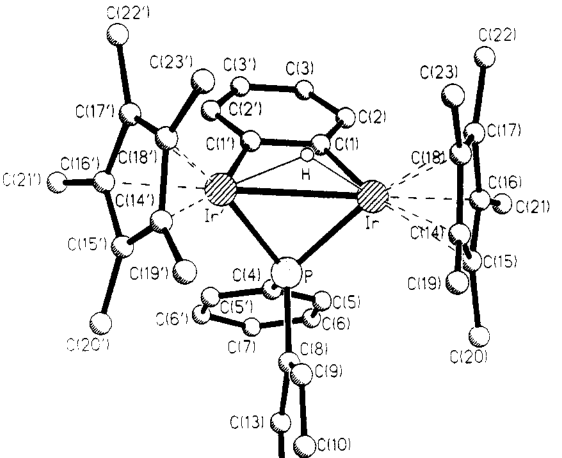


Figure 1. Molecular structure of 2. Selected bond lengths (Å) and bond angles (deg) are as follows: Ir–Ir', 2.8901 (4); Ir–P, 2.263 (2); Ir–C(1), 2.070 (7); Ir–H, 1.83 (8); C(1)–C(1'), 1.40 (1); P–C(4), 1.82 (1); P–C(8), 1.80 (1); ∠Ir–H–Ir', 105 (5); ∠Ir–P–Ir', 79.36 (8); ∠Ir'–Ir–C(1), 68.9 (2).

That 3 is a byproduct of the above reaction and not an intermediate in the formation of 2 was clearly established by noting that 1 and 3 were mixed under the same PTC conditions as above but 2 did not form in the absence of added PPh_3. Note that 3 does not undergo HCl elimination under these PTC conditions.

[†] Present address: Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada K1N 6N5.

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(6) In a typical experiment, a mixture of 1^5 (299 mg; 0.41 mmol), PPh_3 (190 mg; 0.74 mmol), $[PhCH_2NEt_3]^+Cl^-$ (90 mg; 0.4 mmol), benzene (5 mL), and 60% aqueous KOH (5 mL) was vigorously stirred under argon at 20 °C for 8 h. The organic layer was separated and evaporated to dryness, and the residue was washed with hot MeOH (4 × 6 mL) to give reddish orange crystals of **2**: yield 131 mg (35%); mp >250 °C dec. Anal. Calcd for $C_{38}H_{45}Ir_2P$: C, 49.8; H, 5.0. Found: C, 50.1; H, 5.1. ^1H NMR for **2** (200 MHz, cyclohexane-d_{12}, 25 °C): δ −17.7 (d, 1 H, Ir–H–Ir, J(P–H) = 18 Hz), 1.9 (d, 30 H, CH_3, J(P–H) = 1.7 Hz), 6.0 (m, 2 H, 3,6-H), 6.2 (m, 2 H, 4,5-H), 6.8–7.3 (m, 10 H, C_6H_5).

(7) ^1H NMR for **3** (200 MHz, benzene-d_6, 25 °C): δ −13.2 (d, 1 H, Ir–H, J(P–H) = 36.5 Hz), 1.5 (dd, 15 H, CH_3, J(P–H) = 1.9 Hz, J(H–H) = 0.8 Hz), 7.5 (m, 15 H, C_6H_5). Compare this to the spectrum published in: Moseley, K.; Kang, J. W.; Maitlis, P. M. *J. Chem. Soc. A* **1970**, 2875.

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When 1 was allowed to react with PPh_3 in C_6D_6/40% aqueous NaOD/$[PhCH_2NEt_3]^+Cl^-$, no deuterium was incorporated in the product 2; hence, the source of the *o*-phenylene ligand is triphenylphosphine, not the organic phase.

Dehydrochlorination of 1 also occurs in the absence of PPh_3; in this case, however, a complicated mixture results and the ^1H NMR spectrum of the organic phase showed more than 10 different resonances in the hydride region. The intensities of some of these resonances either decreased significantly or disappeared altogether when the reaction was carried out in C_6D_6/60% aqueous KOH/$[PhCH_2NEt_3]^+Cl^-$. This observation indicates that a coordinatively unsaturated, reactive iridium species, formed by the reductive elimination of HCl from 1, reacts with benzene by activating its C-H (C-D) bonds and forming a number of hydrido (deuterido) complexes. It is, then, feasible that the same reactive species is responsible for the formation of 2 when PPh_3 is present in the reaction mixture. Note that the cleavage of P-C bonds in tertiary phosphines by transition-metal complexes often indicates the presence of a coordinatively unsaturated and reactive species.[8] Nonetheless, the mechanism of formation of 2 might be much more complicated than the one suggested above and might involve initial coordination of PPh_3 or OH^- to 1 and cleavage of an Ir-H bond before the elimination of HCl.

The structure of 2 was determined by a single-crystal X-ray diffraction study[9] (Figure 1). Recently, Bergman and co-workers[10] synthesized and completely characterized very similar complexes, $[Ir_2(C_5Me_5)_2(\mu\text{-}OH)(\mu\text{-}PAr_2)(\mu\text{-}C_6H_3R)]$, where Ar = C_6H_5, *p*-$CH_3C_6H_4$ and R = H, CH_3. The molecule 2 occupies a special position on the mirror plane normal to the Ir-Ir′ bond, passing through the phosphorus and hydride atoms. The planes of the bridging ligands in 2, namely Ir-H-Ir′ (A), Ir-P-Ir′ (B), and Ir-C(1)-C(1′)-Ir′ (C), form the pairwise different dihedral angles 156.8 (A/B), 91.4 (B/C), and 111.8° (A/C). The Ir-Ir′ bond (2.8901 (4) Å) is substantially elongated in comparison to that found earlier in the $[Ir_2(C_5H_5)_2(CO)_2(\mu\text{-}C_6H_4)]$ complex (2.717 Å);[11] this is evidently due to the influence of the μ_2-hydride ligand. The Ir···Ir separation in Bergman's related complex $[Ir_2(C_5Me_5)_2(\mu\text{-}OH)(\mu\text{-}PPh_2)(\mu\text{-}C_6H_4)]$ was found to be 3.369 (1) Å.[10] Therefore, the replacement of μ-H for μ-OH in 2 leads to deep structural changes. The geometry of the aromatic nucleus of the phenylene group does not exhibit any noticeable distortions, and its mean plane in fact coincides with the C plane, the corresponding dihedral angle being equal to 1.1°. The Cp* rings, which are planar within 0.01 Å, form a dihedral angle of 129.3°.

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Supplementary Material Available: Full details of the structure solution and tables of atomic coordinates, bond lengths and angles, and thermal parameters (4 pages); a listing of structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

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[8] Garrou, P. E. *Chem. Rev.* **1985**, *85*, 171 and references cited therein.

[9] Crystal data for **2**: $C_{38}H_{45}Ir_2P$, orthorhombic, space group *Pnam*; at +20 °C a = 18.703 (2) Å, b = 11.143 (1) Å, c = 16.247 (1) Å, D_c = 1.799 g/cm^3, and Z = 4; R = 0.032, R_w = 0.036 for 1793 reflections (λ(Mo Kα), graphite monochromator, $\theta/2\theta$ scan); μ = 78.9 cm^{-1}; DIFABS (minimum absorption correction 0.894; maximum absorption correction 1.431; average absorption correction 0.993). All H atoms, including the bridging hydride atom, were located in the difference Fourier synthesis. The position of the hydride ligand was refined isotropically, whereas the remaining hydrogen atoms were included as fixed contributions with B_{iso} = 5.5 Å^2.

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Control of Intramolecular β-Hydrogen Migration in Coordinatively Unsaturated (Diphosphine)platinum Ethyl Cations

Laura Mole and John L. Spencer*

Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, U.K.

Nicholas Carr and A. Guy Orpen*

Department of Inorganic Chemistry, University of Bristol, Bristol BS8 1TS, U.K.

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Summary: Protonation of the complex $[Pt(C_2H_5)_2(\widehat{P\,P})]$ or $[Pt(\eta^2\text{-}C_2H_4)(\widehat{P\,P})]$ ($\widehat{P\,P}$ = $Bu^t_2P(CH_2)_nPBu^t_2$ (n = 2, 3) and *o*-$(Bu^t_2PCH_2)_2C_6H_4$) affords a series of cations characterized as either ethene–hydride or agostic ethyl complexes $[Pt(H)(\eta^2\text{-}C_2H_4)(\widehat{P\,P})]^+$ or $[Pt(C_2H_5)(\widehat{P\,P})]^+$ by NMR spectroscopy and, in the case of $[Pt(C_2H_5)\{Bu^t_2P(CH_2)_3PBu^t_2\}][CB_{11}H_{12}]$, by single-crystal X-ray diffraction. The size of the chelating diphosphine ligand is shown to control the extent of transfer of a hydrogen atom from the β-carbon of the coordinated ethyl group to platinum with the smaller diphosphines favoring transfer to the metal. All the complexes show remarkably low barriers to intramolecular rearrangement.

Complexes with three-center, two-electron M-H-C_β (β-agostic) interactions in their ground states can be viewed as models for intermediates along the migratory insertion/β-elimination pathway.[1] The energy difference between alkene–hydride and alkyl forms is often small, and consequently, some closely related complexes adopt different structures. For example, replacing an ethene by a phosphine ligand in species $[Rh(\text{"}C_2H_5\text{"})(L)(C_5Me_5)]^+$ alters the preferred geometry[1b] from $[Rh(C_2H_5)(C_2H_4)(C_5Me_5)]^+$ to $[Rh(H)(C_2H_4)(PR_3)(C_5Me_5)]^+$.

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