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Reactions of Rh– and Ir–bis(iminophosphoranyl)methanide compounds with electrophiles; a trapped cation–anion complex in the oxidative addition of iodine to a d⁸ metal centre and X-ray crystal structure of [IrI{CH(PPh₂=N-C₆H₄-CH₃-4)₂}(COD)]I, containing two fused four-membered metallacycles $\stackrel{\star}{\sim}$

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Abstract

Reaction of square planar M{CH(PPh₂=N-C₆H₄-CH₃-4)₂)(COD)] (1a: M=Rh; 1b: M=Ir), in which the bis-iminophosphoranylmethanide ligand is bidentate N,C-coordinated, with I₂, MeI and MeOSO₂CF₃ yields products resulting from metal or ligand (N atom) centred reactivity. Complexes 1a and 1b react with MeI and MeOSO₂CF₃ to yield mainly cationic Nmethyl or N,N'-dimethyl derivatives. The reaction of 1b with I₂ results in the selective formation of the hexacoordinate Ir(III) complex (OC-6-43)-[Ir(I) σ -N, σ -N', σ -C-{CH(PPh₂=N-C₆H₄-CH₃-4)₂}(η^2 , η^2 -COD)]⁺I⁻ (4). The molecular structure of 4 has been determined by an X-ray crystal structure study; it crystallizes in space group P2₁/c with a=21.040(2), b=18.399(2), c=26.075(3) Å and β =102.33(2)°. A total of 5243 reflections ($I > 2.5\sigma(I)$) has been used in the refinement which converged, after including a model for observed disorder, to R=0.061 (R_w =0.084). In the cationic part of 4 the N,N',C ligand is facially tridentate coordinated to Ir, thus forming a [2.2.0]-bicyclohexane structure containing an Ir, a C, two P and two N atoms. Iodine is in *trans* position to the methanide carbon atom. Compound 4 represents a trapped cation-anion complex and may be regarded as a model of an intermediate in the polar oxidative addition of I₂ to d⁸ transition metal compounds. Instead of coordinating the second iodine atom, stabilization of 4 is achieved by virtue of the adaptation of the bis(iminophosphoranyl)methanide ligand by coordination of the pendant N atom.

Keywords: Rhodium complexes; Iridium complexes; Iminophosphorane complexes; Oxidative addition; Metallacycle complexes; Crystal structures

1. Introduction

Oxidative addition and reductive elimination reactions are key steps in important catalytic processes, such as hydrogenation and C-C coupling reactions [1]. Therefore much effort has been spent on the elucidation of the characteristics and mechanisms of these types of reactions and several model compounds have been developed to study the intermediates in these reactions. Isolation of intermediates as stable complexes is genarally only possible when ligands are introduced that have specific electronic or structural properties. For example, a few metal-halocarbon complexes have been isolated, i.e. [RhICl(Me)(PPh₃)₂(IMe)] [2], later shown $[RhI_2(Me)(PPh_3)_2]$ [2], cis,trans-[IrH₂(oto be $C_{6}H_{4}I_{2})(PPh_{3})_{2}BF_{4}$ [3], [Ir(COD)(η -o-BrC₆H₄PPh₂)]- SbF_6 [4] and $[IrH_2(IMe)_2(PPh_3)_2]SbF_6$ [5], that may serve as models for intermediates during the early stages of oxidative addition reactions of alkylhalogenides. Also, complexes of the type $[PtR(\eta^{1} I_2$ (C₆H₃(CH₂NMe₂)₂-O,O'] in which the I_2 molecule is η^1 coordinated are known [6,7]. The oxidative addition of I_2 to the metal centre proceeds via an $S_N 2$ mechanism

^{*} This paper is dedicated to the memory of Professor Ugo Croatto. * Corresponding author.

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and the initial step has convincingly been shown to be the formation of a complex in which I_2 is end-on coordinated to Pt. Further reaction proceeds probably via an intermediate cation-anion complex of the type $[Pt(R)I\{C_6H_3(CH_2NMe_2)_2-O,O'\}]^+I^-$ to give the oxidative addition product $[PtR(I)_2\{C_6H_3(CH_2NMe_2)_2-O,O'\}]$.

In fact, cation-anion complexes in reactions of mononuclear d⁸ metal complexes with iodine have, to our knowledge, never been isolated [8a]. A related ionic complex, *fac*-[PtMe₃(SMe₂)₂(NCCD₃)]⁺1⁻, occurring in the oxidative addition of MeI to *cis*-[PtMe₂(SMe₂)₂], has been characterized [8b]. This intermediate eventually reacts further to give the oxidative addition complex *fac*-[Pt(IV)IMe₃(SMe₂)₂]. Ionic triorganoplatinum(IV) compounds containing rigid bidentate nitrogen ligands have also been authenticated [8c].

In another paper we reported on rhodium(I) and iridium(I) complexes bearing a bis(iminophosphoranyl)methanide ligand, i.e. $[M{CH(PPh_2=N-R')_2}L_2]$ (1), in which the ligand is coordinated as a σ -N, σ -C chelate [9]. It was anticipated that, as a result of the presence of a second, uncoordinated iminophosphorane group in 1, in metal centred reactions with, for example, HX, MeX or X₂, the bis(iminophosphoranyl)methanide ligand could adopt other coordination modes, such as σ -N, σ -N' bidentate or σ -N, σ -N', σ -C terdentate coordination. In fact a terdentate coordination mode has been suggested to occur as an intermediate complex formed in the reaction of the Rh(I) and Ir(I) complexes 1 with HCl. It has been found that initially an oxidative



addition of HCl to the metal centre with formation of an M(III)-hydride intermediate occurred, which reacted further via migration of the hydrogen atom to either the iminophosphorane N atom or the methanide C atom to yield 2 or 3, respectively (Eq. (1)) [9]. Based on ¹H and ³¹P NMR chemical shift data, a structure in which the bis(iminophosphoranyl)methanide ligand has adopted a *fac* σ -N, σ -N', σ -C coordination mode could be assigned to the intermediate M(III) complex.

In this paper we describe the reactions of the bis(iminophosphoranyl)methanide complexes [M{CH- $(PPh_2 = N-p-tolyl)_2 (COD) (M = Rh (1a); Ir (1b))$ with I_2 and MeX (X=I, OSO₂CF₃). It will be shown that in the reaction of $[Ir{CH(PPh_2=N-p-tolyl)_2}(COD)]$ (1b) with iodine the new, hexacoordinate $[Ir(III)I{CH(PPh_2=N-p-tolyl)_2}(COD)]I$ is formed, in which the bis(iminophosphoranyl)methanide ligand is coordinated in a unique fac-terdentate mode. This compound represents an isolated ionic complex, mimicking the situation halfway a polar oxidative addition reaction of iodine to a d⁸ transition metal compound.

2. Experimental

All reactions were performed under an atmosphere of dry, purified nitrogen using standard Schlenk techniques. All solvents were carefully dried and distilled prior to use. $[Rh{CH(PPh_2=N-p-tolyl)_2}(COD)]$ (1a) and $[Ir{CH(PPh_2=N-p-tolyl)_2}(COD)]$ (1b) were synthesized according to literature procedures [9].

Elemental analyses were carried out by the section Elemental Analysis of the Institute for Applied Chemistry, ITC/TNO, Zeist, Netherlands. Field desorption (FD) mass spectra were obtained with a Varian MAT711 double focusing mass spectrometer, and were performed by the Institute for Mass Spectroscopy of the University of Amsterdam. ¹H and ¹³C NMR spectra were recorded either on a Bruker AC100 or a Bruker WM250 spectrometer. ³¹P NMR spectra were obtained with a Bruker WP80 or a Bruker AC100 spectrometer. Chemical shifts are in ppm relative to SiMe₄ for ¹H and ¹³C spectra and to 85% H₃PO₄ for ³¹P spectra, with shifts to high frequency positive. Coupling constants are in Hz. IR spectra were recorded with a Perkin-Elmer 283 spectrophotometer.

2.1. Reaction of $[Ir{CH(PPh_2=N-p-tolyl)_2}(COD)]$ (1b) with I_2

To a solution of ~0.05 mmol $[Ir{CH(PPh_2=N-p-tolyl)_2}(COD)]$ (1b) in 15 ml Et₂O was slowly added 1 equiv. of I₂ in 5 ml Et₂O at room temperature. After 1 h a red precipitate had formed, which was filtered off, washed with Et₂O (2×10 ml) and pentane (2×10 ml) and dried in vacuo giving red $[IrI{CH(PPh_2=N-p-tol)]}$

tolyl)₂}(COD)]I (4) in 95% yield. Orange-red crystals suitable for X-ray structure determination were obtained by slow diffusion of hexane into a solution of 4 in a CH₂Cl₂/hexane mixture (\sim 5:1) at room temperature.

³¹P NMR (CD₂Cl₂): 61.5 ppm. ¹H NMR (CD₂Cl₂): 2.09–2.12 (m, CH₂, COD, 4H); 2.33–2.37 (m, CH₂, COD, 2H); 2.34 (CH₃, tolyl, 6H); 2.59–2.63 (m, CH₂, COD, 2H); 3.34 (m, =CH, COD, 2H); 4.78 (m, =CH, COD, 2H); 5.07 (t, ²J(P,H) = 2.6 Hz, P–CH–P, 1H); 6.96 + 7.10 (d, ³J(H,H) = 7.9 Hz, tolyl, 8H); 6.87–6.94 (m, *m*-Ph, 8H); 7.29–7.37 (m, *p*-Ph, 4H); 7.74 (br, *o*-Ph, 6H); 8.31 (br, *o*-Ph, 2H). IR (KBr): ν (P–N) = 1273 cm⁻¹. FD mass found: *m*/*z* = 1021 (*M*⁺; calc. for C₄₇H₄₇IIrN₂P₂: *M* = 1020.959); 894 (=(*M*-I)⁺). Anal. Found: C, 49.54; H, 4.29; N 2.40. Calc.: C, 49.18; H, 4.13; N, 2.44%.

2.2. Reaction of $[M{CH(PPh_2=N-p-tolyl)_2}(COD)]$ (1a, b) with MeOTf to give $[M{p-tolyl-N=PPh_2-CH-PPh_2-N(Me)(p-tolyl)}(COD)]OTf$ (5a, b)

(a) To a solution of 0.1 mmol $[M{CH(PPh_2=N-p-tolyl)_2}(COD)]$ (1a,b) in 10 ml benzene 1 equiv. of MeOSO₂CF₃ (MeOTf) was added. After stirring for 2 h the solvent was evaporated to dryness. The residue was washed with pentane (2×4 ml) and dried in vacuo, giving $[M{p-tolyl-N=PPh_2-CH-PPh_2-N(Me)(p-to-lyl)}](COD)]OTf$ (5a,b) in 95% yield.

[Rh{p-tolyl-N=PPh₂-CH-PPh₂-N(Me)(p-tolyl)}-(COD)]OTf (5a): ³¹P NMR (C₆D₆): 19.7 (br d, ²J(Rh,P)=14.6 Hz; ²J(P,P) < 2 Hz); 44.4 (br, ²J(Rh,P), ²J(P,P) < 2 Hz). ¹H NMR (C₆D₆): 1.1-1.3 (CH₂, COD); 1.5-1.8 (CH₂, COD); 1.84 (CH₃, tolyl); 1.92 (CH₃, tolyl); 2.58 (d, ³J(P,H)=9.5 Hz, N-CH₃); 3.75 (=CH, COD, 2H); 3.79 (br d, ²J(P,H)=15.2 Hz, ²J(P,H), ²J(Rh,H) < 1 Hz, P-CH-P); 4.15 (=CH, COD, 1H); 4.86 (=CH, COD, 1H); 6.28+6.63 (d, 7.8 Hz, tolyl); 6.81+6.93 (d, 7.8 Hz, tolyl); 7.0-7.2 (m, m-Ph, p-Ph); 7.30 (m, m-Ph, p-Ph); 7.45 (m, m-Ph); 7.67 (m, p-Ph); 8.16-8.24 (m, o-Ph); 8.44-8.53 (m, o-Ph); 8.63-8.70 (m, o-Ph). Anal. Found: C, 61.20; H, 5.20; N, 3.21. Calc.: C, 60.75; H, 5.20; N, 2.89%. FD mass found: m/z = 968 (M^+ ; calc. for C₄₉H₅₀F₃N₂O₃P₂RhS: M = 968.861).

[Ir{p-tolyl-N=PPh₂-CH-PPh₂-N(Me)(p-tolyl)}-(COD)]OTf (**5b**): ³¹P NMR (C₆D₆): 34.7 (d, ²J(P,P) = 2.0 Hz); 46.5 (d, ²J(P,P) = 2.0 Hz). ¹H NMR (C₆D₆): 1.5–1.8 (CH₂, COD, 4H); 1.80 (CH₃, tolyl); 1.94 (CH₃, tolyl); 2.0–2.2 (CH₂, COD, 2H); 2.5–2.7 (CH₂, COD, 2H); 2.67 (d, ³J(P,H) = 9.6 Hz, N–CH₃); 3.47 (=CH, COD, 2H); 3.94 (=CH, COD, 2H); 4.69 (dd, ²J(P,H) = 17.4 Hz, ²J(P,H) = 1.7 Hz, P–CH–P); 6.30+6.65 (d, 8.0 Hz, tolyl); 6.75+6.90 (d, 8.1 Hz, tolyl); 7.0–7.3 (m, m-Ph, p-Ph); 7.6 (m, p-Ph); 8.18–8.48 (m, o-Ph). Anal. Found: C, 55.89; H, 4.86; N, 2.97. Calc.: C, 55.62; H, 4.76; N, 2.65%. FD mass found: m/z=909 (M^+ ; calc. for C₄₈H₅₀IrN₂P₂: M=909.09 for M–OTf). (b) To a solution of ~0.05 mmol **1a** or **1b** in 3 ml benzene a fivefold excess of MeOTf was added at room temperature. After stirring for 24 h a brown oil had separated. After addition of 10 ml Et₂O a brown residue was filtered off, washed with 5 ml Et₂O and dried in vacuo. The residue consisted, according to FD mass spectroscopy, as well as ¹H and ³¹P NMR, of $[Ch_2(PPh_2-NMe-p-tolyl)(PPh_2-NH-p-tolyl)]^{2+}$ and $[CH_2(PPh_2-NH-p-tolyl)_2]^{2+}$ [10].

 $[CH_{2}(PPh_{2}-NMe-p-tolyl)(PPh_{2}-NH-p-tolyl)]^{2+}: {}^{1}H$ NMR (CDCl₃): 2.08 (CH₃, tolyl, 6H); 3.37 (d, {}^{3}J(P,H) = 9.9 Hz, N-CH₃, 3H); 5.36 (t, {}^{2}J(P,H) = 15.6 Hz; P-CH_{2}-P, 2H); 6.44 (d, 8.4 Hz, tolyl, 2H); 6.75 (d, 8.8 Hz, tolyl, 2H); 6.79 (d, 8.4 Hz, tolyl, 2H); 6.90 (d, 8.8 Hz, tolyl, 2H); 7.29-7.91 (m, Ph, 20H); 8.15 (d, 9.6 Hz, N-H, 1H). {}^{31}P NMR (CDCl₃): 30.0 (d); 41.8 (d); {}^{2}J(P,P) = 12.4 Hz. FD mass found: m/z = 759 ([CH₂(PPh₂-NMe-p-tolyl)(PPh₂-N-p-tolyl)]OTf), 609 ([CH₂(PPh₂-NMe-p-tolyl)(PPh₂-N-p-tolyl)]).

The yellow filtrate of the reaction of **1b** with MeOTf contained, according to ¹H and ³¹P NMR, $[CH_2(PPh_2-NMe-p-tolyl)(PPh_2-NH-p-tolyl)]^{2+}$, $[CH_2(PPh_2-NH-p-tolyl)_2]^{2+}$ [10] and [Ir(COD)(OTf)] [11]. [Ir(COD)-(OTf)]: ¹H NMR (CDCl₃): 1.9–2.2 (m, 8H); 4.70 (m, 4H).

2.3. Reaction of $[Rh(COD){CH(PPh_2=N-p-tolyl)_2}]$ (1a) with MeI to give $[CH(PPh_2-NMe-p-tolyl)_2]I$ (6) and $[RhI(COD)]_2$

A solution of 138.2 mg 1a (0.17 mmol) and 100 μ l MeI (1.6 mmol) in 7 ml benzene was heated at 358 K for 3 h. After cooling down to room temperature 15 ml of pentane were added. The precipitate was filtered off, washed with pentane (2×10 ml) and dried in vacuo giving brown [CH(PPh₂-NMe-*p*-tolyl)₂]I (6) in ~80% yield.

[CH(PPh₂-NMe-p-tolyl)₂]I: ¹H NMR (CD₂Cl₂): 1.71 $(t, {}^{2}J(P,H) = 9.9 \text{ Hz}, P-CH-P, 1H); 2.30 (CH_{3}, tolyl,$ 6H); 2.91 (vt, N-CH₃, 6H); 6.82 + 7.03 (d, ${}^{3}J$ (H,H) = 7.9 Hz, tolyl, 8H); 7.16-7.24 (m, m-Ph, 8H); 7.33-7.42 (m, o-Ph, 8H); 7.57–7.62 (m, p-Ph, 4H). ¹³C NMR (CD₂Cl₂): 12.6 (t, ${}^{1}J(P,C) = 149$ Hz, P-CH-P); 41.0 (vd, 2.5 Hz, N-CH₃), p-tolyl: 21.0 (CH₃); 128.1 (Cortho); 130.3 (Cmeta); 136.9 (Cpara); 141.6 (Cipso); phenyl: 126.8 (d, 112.3 Hz, Cipso); 129.4 (vt, 6.5 Hz, Cmeta); 132.7 (vt, 5.3 Hz, Conho); 133.2 (C_{para}). ³¹P NMR (CD₂Cl₂): 39.2 ppm. IR (KBr): ν (P-N) = 1263 cm⁻¹. FD mass found: m/z = 623 (M^+), 608 ($(M - CH_3)^+$); calc. for $C_{41}H_{41}N_2P_2$: M = 623.741. Anal. Found: C, 64.44; H, 5.40; N, 3.70. Calc.: C, 64.60; H, 5.51; N, 3.73%. The filtrate, according to ¹H and ³¹P NMR, consisted of unreacted 1a, [CH(PPh₂-NMe-p $tolyl_{2}I$ (6) and $[RhI(COD)]_{2}$ [12]. $[RhI(COD)]_{2}$: ¹H NMR (CDCl₃): 1.54–1.78 (m, CH₂, COD); 2.33–2.47 $(m, CH_2, COD); 4.64 (m, =CH, COD).$

2.4. Reaction of $[Ir{CH(PPh_2=N-p-tolyl)_2}(COD)]$ (1b) with MeI to give $[CH(PPh_2-NMe-p-tolyl)_2]I$ (6) and $[IrI(COD)]_2$

(a) A solution of 200 mg 1b (0.22 mmol) and 2 ml MeI (~32 mmol) in 10 ml benzene was refluxed for 6 h. After cooling down to room temperature a small amount of white precipitate had formed in an orange-red solution. The white powder was filtered off, washed with Et₂O and pentane, and dried in vacuo. The filtrate was evaporated to dryness in vacuo, washed with Et₂O and pentane, and dried in vacuo giving an orange-red powder. ³¹P NMR (C₆D₆): -7.1 (d), +52.1 (d); ²J(P,P)=17.1 Hz (~40%); -6.2 (d), +55.8 (d); ²J(P,P)=17.1 Hz (~30%); 47.5 (30%). FD mass found: m/z=894 (1b); 908 (M^+ ; calc. for C₄₈H₅₀IrN₂P₂: M=909.09). The filtrate, according to ¹H and ³¹P NMR, consisted of unreacted 1b, [CH(PPh₂-NMe-p-tolyl)₂]I (6) and [IrI(COD)]₂.

(b) A mixture of 7.6 mg **1b** (8.5 mmol) and 5 ml MeI (80.2 mmol) in 0.4 ml C_6D_6 in a 5 mm NMR tube was irradiated with a quartz filtered Hg lamp for 30 min at room temperature. After heating this mixture at 323 K for 30 min, according to ³¹P NMR, one phosphorus containing product was formed (at 47.8 ppm). Workup of the reaction product gave decomposition reactions, as evidenced by the formation of [CH(PPh₂-NMe-*p*-tolyl)₂]I (6), [IrI(COD)]₂ and free COD (¹H and ³¹P NMR).

2.5. Structure determination and refinement of 4

An orange-red needle shaped crystal was glued on top of a glass-fibre and transferred to an Enraf-Nonius CAD4F diffractometer for data collection. Unit cell parameters were determined from a least-squares treatment of the SET4 setting angles of 25 reflections with $9.2 < \theta < 14.2^{\circ}$. The crystal reflected poorly and showed broad reflection profiles. The unit cell parameters were checked for the presence of higher lattice symmetry [13]. Data were corrected for Lp, for a linear decay (3.9%) of the intensity control reflections during the 95 h of X-ray exposure time and for absorption (Gaussian integration). The heavy atoms (Ir, I) were located with direct methods (SHELXS86) [14]; all other non-H atoms were located from a series of subsequent difference Fourier maps. Refinement on F was carried out by full-matrix least-squares techniques. H atoms were introduced on calculated positions (C-H=0.98 Å) and included in the refinement riding on their carrier atoms. In view of the rather poor crystal quality and the relatively small number of significant reflections, only the Ir, I and P atoms were refined with anisotropic thermal parameters. The C and N atoms were refined with isotropic thermal parameters, and the H atoms with one common isotropic thermal parameter $(U=0.09(1) \text{ Å}^2)$. Eight hexane solvate and four dichloromethane solvate molecules located in a large cavity of approximately 2000 Å³ could not be located from difference Fourier maps unambiguously and were taken into account in the structure factor and refinement calculations by direct Fourier transformation of the electron density in the cavity, following the BYPASS procedure [15]. An electron count of the electron density in the void is consistent with the interpretation given. The structure was found to be disordered in a ratio of 94.3(3)%/5.7(3)% as indicated by a difference Fourier map showing residual density peaks corresponding to Ir and I atoms in alternatively oriented molecules. Due to the poor resolution of the data set, only the heavy atoms (Ir, I) could be refined with a disorder model; the disorder effect of 5.7(3)% is irresolvable for the lighter P, N and C atoms. Weights were introduced in the final refinement cycles; convergence was reached at R = 0.061. Crystal data and numerical details of the structure determination are given in Table 1. Neutral atom scattering factors were taken from Ref. [16] and corrected for anomalous dispersion [17]. All calculations were performed with SHELX76 [18] and the EUCLID package [19] (geometrical calculations and illustrations) on a MicroVAX cluster.

3. Results

Reaction of the Rh and Ir complexes $[M(COD)\{\sigma$ - N,σ -C-CH(PPh₂=N-p-tolyl)₂] (M=Rh (1a); Ir (1b)) with the electrophilic reagents I₂, MeOTf or MeI gave rise to both metal and ligand centred reactivity. In the reaction of 1b (M=Ir) with I₂ the new complex $[M(COD)I\{\sigma$ - N,σ - N',σ -C-CH(PPh₂=N-p-tolyl)₂]I (4) is formed, in which the bis(iminophosphoranyl)-methanide ligand has adopted a terdentate coordination mode.

Reaction of 1 with MeOTf proceeds via direct methylation of the nitrogen atom of the pendant iminophosphorane group to yield complexes of the type $[M(COD)(p-tolyl-N=PPh_2-CH-PPh_2-NMe-p-tolyl)]$ -OTf (5). When employing MeI as the reagent, reaction with the bis(iminophosphoranyl)methanide ligand as well as with the metal occurred.

3.1. Reaction with I_2

The reaction of 1a (M = Rh) with I_2 in diethyl ether or benzene gave irreproducible results. During this reaction several (decomposition) products were formed, as evidenced by an intense blackening of the mixture during the reaction in benzene, and the formation of several organophosphorus compounds. Isolation of either of these products failed due to further decomposition reactions.

Table 1

Crystal data and details of the structure determination of $[Ir(COD)I\{CH(PPh_2=N-C_6H_4-CH_3-4)_2\}]I$ (4)

Crystal data	
Formula	$C_{47}H_{47}N_2P_2I_2Ir \cdot C_6H_{14} \cdot \frac{1}{2}CH_2Cl_2$
Molecular weight	1276.51
Space group	$P2_1/c$ (No. 14)
Crystal system	monoclinic
a (Å)	21.040(2)
b (Å)	18.399(2)
c (Å)	26.075(3)
β (°)	102.33(2)
V (Å ³)	9861(2)
Ζ	8
$D_{\text{calc}} (\text{g cm}^{-3})$	1.720
F(000)	5016
$\mu (\rm cm^{-1})$	42.9
Crystal size (mm)	$0.50 \times 0.25 \times 0.12$
Data collection	
Radiation (Å)	Mo K α (Zr-filtered), 0.71073
$\theta_{\min}, \ \theta_{\max}$ (°)	0.80, 21.50
<i>T</i> (K)	100
Scan type	ω/2θ
Δω (°)	$0.70 + 0.35 \tan \theta$
Horizontal and vertical aperture (mm)	3.0, 3.0
Distance crystal to detector (mm)	173
Reference reflections	0 4 1, -2 0 2
Data set	$-21 \le h \le 0, \ 0 \le k \le 18, \ -25 \le l \le 26$
Total data	11789
Total unique data	11293
Observed data	5243 $(I > 2.5\sigma(I))$
Refinement	
No. refined parameters	501
Weighting scheme	$w = 1.0/(\sigma^2(F) + 0.005284F^2)$
Final R, wR values	0.061, 0.084
$(\Delta/\sigma)_{\rm sv}$ in final cycle	0.015
Residual density: min., max. (e $Å^{-3}$)	- 1.52, 1.50



However, reaction of 1b (M=Ir) with an equimolar quantity of slowly added I_2 in diethyl ether at room temperature proceeded very cleanly to give one single product (4) in 95% yield (Eq. (2)).

The molecular structure of this new compound 4, which analyzed correctly for $[IrI_2\{CH(PPh_2=N-p-to-lyl)_2\}(COD)]$, was elucidated by ¹H and ³¹P NMR, IR, FD mass spectroscopy and a single crystal X-ray structure determination. Performing the reaction with a molar ratio I₂:1b higher than 1:1 the same organoiridium species was formed (IR, ¹H and ³¹P NMR). In this case the product contained, according to elemental analysis, more iodine than in the 1:1 reaction, which is most probably a result of the formation of I_3^- or I_5^- anions by reaction of the I^- anion with excess I_2 [20].

Compound 4 is not soluble in apolar solvents such as alkanes and Et_2O , slightly soluble in benzene and quite soluble in dichloromethane, chloroform and THF. It is thermally stable in moist air for at least 2 months. In solution, 4 is configurationally stable (e.g. in toluene at 373 K it neither isomerizes nor does it coordinate the external iodide at the expense of one of the coordinated ligands), but slow decomposition is observed in CDCl₃ solution, which is complete within 4 days.

In the IR spectrum of 4 (KBr pellet) a strong band is observed at 1273 cm⁻¹, a value indicative of ν (P=N) of an iminophosphorane group within a four-membered metallacycle, since it is close to the values found for other four-membered metallo-iminophosphoranylmethanide complexes, e.g. 1294 and 1287 cm⁻¹ for [Rh(CH₂PPh₂=N-p-tolyl)L₂] (L₂=COD and (CO)₂, respectively) [21] or 1285 and 1279 cm⁻¹ for $[Ir{CH(PPh_2=N-p-tolyl)_2}L_2]$ (1, $L_2=COD$ and $(CO)_2$, respectively) [9b].

In the ¹H NMR spectrum of 4 (CD₂Cl₂) the resonance of the methanide proton is found at 5.07 ppm, split into a triplet (²J(P,H)=2.6 Hz) due to coupling with two equivalent phosphorus nuclei. For the two *p*-tolyl groups only one methyl signal at 2.34 ppm and one pair of doublets in the aryl region are found, indicating that these groups are isochronous. The COD olefinic hydrogen atoms are found as two broad resonances at 3.34 and 4.78 ppm. In the ³¹P NMR spectrum only one signal is found for both phosphorus atoms at 61.5 ppm over the temperature range 193–373 K.



These NMR data indicate that the bis(iminophosphoranyl)methanide ligand is symmetrically coordinated to the Ir atom and, by the observation of two signals for the olefinic COD hydrogen atoms, that 4 should have at least C_s symmetry in solution. These symmetry considerations are in agreement with a structure of 4 in which the bis(iminophosphoranyl)methanide has adopted a terdentate facial o-N,o-N',o-C coordination mode. Another structure, in which the ligand is σ -N, σ -N' bidentate coordinated (4') albeit in agreement with these symmetry requirements, is not in agreement with the details of the NMR data. (Coordination modes such as in 4' are known for complexes with related ligands, see Refs. [22-24].) It was anticipated that the bis(iminophosphoranyl)methanide ligand in 4 has a terdentate coordination mode in solution, since (i) for a bidentate coordination mode as in 4' the methanide proton should have considerable ylide character [22] and is expected to resonate at much lower frequencies in the ¹H NMR spectrum than the observed value of 5.07 ppm in 4, e.g. 1.90 ppm in $[WCl_3[NPPh_2CHPPh_2N]]$ [22a] or in the range from -0.36 to 0.23 ppm in bis(methylenephosphoranyl)methanide complexes [23], and (ii) the ³¹P chemical shift of 61.5 ppm is indicative of an iminophosphorane phosphorus nucleus in a fourmembered metallacycle [9b,21], whereas the ³¹P resonance of complex 4' is expected at lower frequencies, based on the chemical shifts of, for example, [WCl₃{NPPh₂CHPPh₂N}] at 15.5 ppm [22a], [PtCl {C(PPh₂S)₃}(PEt₃)] at 25.32 and 35.29 ppm [25], $[Pt{C(PPh_2S)_3}(PEt_3)_2]$ at 32.40 and 39.50 ppm [25], $[M{CH(PPh_2S)_2}(COD)]$ for M = Rh at 36.0 ppm and for M=Ir at 34.1 ppm [24] or bis(methylenephosphoranyl)methanide complexes (10.2-13.8 ppm)

[22,23]. Our expectations were confirmed by an X-ray crystal structure analysis of 4.

3.2. Molecular structure of $[IrI{CH(PPh_2=N-p-tolyl)_2}-(COD)]^+I^-$ (4)

The unit cell of the title compound consists of eight discrete molecules of 4 and voids containing disordered solvents of crystallization. The asymmetric unit comprises two crystallographically independent cations, two iodide anions, one molecule of CH_2Cl_2 and two hexane molecules. The molecular structure of one cation is shown in Fig. 1. Selected bond distances and angles for both molecules are given in Tables 2 and 3. Fractional coordinates and equivalent isotropic thermal parameters are given in Table 4. Unless the data differ by more than 2σ , only molecule 1 will be described.

The most important feature of the structure of **4** is the terdentate facial coordination mode of the bis(iminophosphoranyl)methanide ligand to Ir, forming two fused four-membered Ir-N-P-C metallacycles sharing the Ir-C vertex. The coordination geometry around Ir is distorted octahedral, with the two axial positions taken by the iodide atom and the methanide C atom of the bis(iminophosphoranyl)methanide ligand. The equatorial sites are taken by the two N atoms of this ligand and the two olefinic bonds of the COD ligand (with M1 and M2 being the midpoints of C40-C41 and C44-C45, respectively). The molecule has an approximate mirror plane, defined by the atoms C1, Ir and I.

The most striking deviations from octahedral geometry are the I-Ir-C1 angle of $151.8(7)^{\circ}$ and the acute C1-Ir-N angles of 70.0(9) and $71(1)^{\circ}$, and may be attributed to constraints within the two four-membered



Fig. 1. Thermal ellipsoid plot (40% probability) of the cation of $[IrI{CH(PPh_2=N-C_6H_4-CH_3-4)_2}(COD)]^+I^-$ (4). Hydrogen atoms have been omitted for clarity and only one of the nearly identical unique cations is shown.

Table 2

Selected interatomic bond distances (Å) of the cationic part of $[Ir(COD)I\{CH(PPh_2=N-C_6H_4-CH_3-4)_2\}]I$ (4) with standard deviations in parentheses

	Molecule 1	Molecule 2
Around Ir		
Ir–N1	2.14(2)	2.14(2)
Ir–N2	2.13(2)	2.16(2)
Ir–C1	2.22(3)	2.23(3)
IrI	2.713(2)	2.723(2)
Ir-M1	2.13(3)	2.09(3)
IrC40	2.23(3)	2.23(3)
Ir-C41	2.24(3)	2.18(3)
Ir-M2	2.14(3)	2.09(3)
IrC44	2.24(3)	2.21(3)
IrC45	2.27(3)	2.19(3)
Within ligand		
N1-C2	1.49(4)	1.46(3)
N1-P1	1.56(2)	1.60(2)
P1C1	1.83(3)	1.81(3)
P1-C16	1.77(3)	1.80(3)
P1-C22	1.75(3)	1.81(2)
N2C9	1.40(4)	1.45(3)
N2-P2	1.61(2)	1.61(2)
P2C1	1.79(3)	1.85(3)
P2-C28	1.73(3)	1.83(3)
P2-C34	1.81(3)	1.80(3)
Within COD		
C40-C41	1.33(4)	1.45(4)
C44C45	1.40(4)	1.38(4)
$\langle C_{sp2} - C_{sp3} \rangle$	1.51(4)	1.55(4)
$\langle C_{sp3} - C_{sp3} \rangle$	1.46(4)	1.48(4)

metallacycles. The C1-M-N angles are even smaller than those found in other complexes containing M-N-P-C metallacycles, i.e. $73.1(1)^{\circ}$ in [Rh(p-tolyl-N=PPh₂-CH-PPh₂-NH-p-tolyl)(COD)] (2) [9a], $74.2(2)^{\circ}$ in [Rh(CH₂PPh₂=N-p-tolyl)(COD)] or $73.4(4)^{\circ}$ [21] in [Ir{CH(PPh₂=N-p-tolyl)₂}(COD)] (1b) [9b].

The P-N bond distances of 1.56(2) and 1.61(2) Å fall well within the range usually found for coordination complexes of iminophosphoranes [9,21,26] and also the Ir-N distances of 2.14(2) and 2.13(2) Å are normal values [27]. The Ir-C1 and Ir-I bond lengths are within the ranges normally observed [3,5,28,29]. The cyclo-1,5-octadiene ligand is coordinated in its standard twisted boat conformation and is bent away from the bulky iodide, as evidenced by the deviation of the angles between the olefinic bonds and the coordination plane (88(1) and 85(1)°) from the ideal 90°.

The observed facial terdentate coordination mode of the bis(iminophosphoranyl)methanide ligand is unprecedented; two fused four-membered metallacycles sharing the M-C vertex are present within one monomeric complex. The scarcity of such complexes is not surprising, because such a system is expected to be rather unstable as a result of the presence of two strained four-membered metallacycles in a metalladi-

Around Ir		
N1–Ir–N2	85.7(8)	87.2(8)
N1-Ir-C1	70.0(9)	70.5(9)
N1IrI	89.8(6)	89.0(6)
N1–Ir–M1	171.2(9)	173.3(9)
N1–Ir–M2	95.7(9)	93(1)
N2-Ir-C1	71(1)	71.8(9)
N2–Ir–I	88.6(6)	88.6(6)
N2–Ir–M1	92.4(9)	93.3(9)
N2–Ir–M2	174(1)	175(1)
C1–Ir–I	151.8(7)	151.8(7)
C1–Ir–M1	101(1)	103(1)
C1–Ir–M2	104(1)	103(1)
I-Ir-M1	98.8(7)	97.7(7)
I-Ir-M2	97.1(8)	96.6(8)
M1–Ir–M2	85(1)	86(1)
Within ligand		
IrN1P1	101(1)	101(1)
IrN1C2	125(2)	127(2)
P1-N1-C2	129(2)	127(2)
N1-P1-C1	95(1)	95(1)
N1-P1-C16	120(1)	123(1)
N1-P1-C22	114(1)	112(1)
C1-P1-C16	109(1)	108(1)
C1-P1-C22	120(1)	120(1)
C16-P1-C22	101(1)	101(1)

N1-P1-C22	114(1)	112(1)
C1-P1-C16	109(1)	108(1)
C1-P1-C22	120(1)	120(1)
C16-P1-C22	101(1)	101(1)
P1–C1–Ir	90(1)	91(1)
P1-C1-P2	114(2)	115(1)
Ir-N2-P2	100(1)	99(1)
Ir-N2-C9	131(2)	127(2)
P2-N2-C9	127(2)	128(2)
N2-P2-C1	96(1)	96(1)
N2-P2-C28	116(1)	113(1)
N2-P2-C34	119(1)	120(1)
C1-P2-C28	120(1)	119(1)
C1-P2-C34	107(1)	111(1)
C28-P2-C34	101(1)	100(1)
P2–C1–Ir	91(1)	90(1)
Within COD		
$\langle C_{sp2} - C_{sp2} - C_{sp3} \rangle$	123(2)	122(3)
$\langle C_{sp3} - C_{sp3} - C_{sp2} \rangle$	118(3)	116(2)

azabicyclo[2,2,0]hexane structure. In 4 the strain in the M-N-P-C rings is most probably minimized by a narrowing of the N-P-C angle, the angles at the phosphorus atom being adaptable as a result of available d-orbitals. As a consequence, the M-N-P and M-C-P angles will be less acute, thus releasing some of the ring strain. Indeed it was found that the N-P-C angles are somewhat smaller and the M-N-P and M-C-P angles larger than the corresponding angles in other iminophosphoranylmethanide complexes [9,21].

Although several types of terdentate ligands are known, they often concern systems that give five- or six-membered rings upon coordination, these being the

Molecule 2

Table 3 Selected interatomic bond angles (°) of the cationic part of $[Ir(COD){CH(PPh_2=N-C_6H_4-CH_3-4)_2}]I(4)$ with standard deviations in parentheses

Molecule 1

Table 4 Final coordinates and equivalent isotropic thermal parameters and their e.s.d.s. in parentheses for A

Table	4	(continued)
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their e.s.d.s in parentheses for 4			Atom	x	у	z	U_{eq} or		
Atom	x	у	z	$U_{eq} = 0r$ $U_{eq} = (Å^2)$	Molecul	e ?			U _{iso} (A [*])
				0 130 (11)	Ir ^b	-0.04907(6)	0.06282(6)	0.21581(5)	0.0103(4)
12	0.6622(1)	0.0707(2)	0.1240(1)	0.062(1)	I1 b	0.07472(9)	0.0366(1)	0.26943(8)	0.0164(7)
I3	0.1652(1)	0.2724(2)	0.1366(1)	0.074(1)	P1	-0.0786(3)	0.0894(4)	0.1039(3)	0.023(3)
Malagu	la 1				P2	-0.0934(3)	0.2082(4)	0.1842(3)	0.018(3)
Molecu		0 20722/6)	0 22045(5)	0.0160(4)	N 1	~0.014(1)	0.064(1)	0.1445(8)	0.015(5)
11 b	0.43114(0) 0.57708(0)	0.29732(0)	0.22043(3)	0.0109(4)	N2	-0.028(1)	0.178(1)	0.2217(8)	0.019(6)
P1	0.37708(3)	0.3214(1) 0.1550(4)	0.20835(8)	0.0232(7)	C1	-0.121(1)	0.120(1)	0.154(1)	0.021(7)
P2	0.4033(3)	0.1330(4)	0.1023(3)	0.024(3)	C2	0.040(1)	0.021(1)	0.1327(9)	0.007(6)
N1	0.4117(4)	0.184(1)	0.1005(5)	0.020(5)	C3	0.034(1)	-0.051(2)	0.117(1)	0.031(8)
N2	0.472(1)	0.104(1)	0.1467(9)	0.027(6)	C4	0.087(1)	-0.090(2)	0.105(1)	0.032(8)
CI	0.375(1)	0.245(1)	0.1407(2)	0.027(0)	C5	0.147(1)	-0.056(1)	0.114(1)	0.025(7)
C2	0.575(1)	0.243(1)	0.152(1)	0.045(9)	C6	0.205(1)	-0.091(1)	0.101(1)	0.026(7)
C3	0.527(2)	0.144(2)	0.22(1)	0.031(8)	C7	0.152(1)	0.016(1)	0.131(1)	0.017(7)
C4	0.517(2)	0.086(2)	0.337(1)	0.027(7)	C8	0.099(1)	0.060(1)	0.142(1)	0.020(7)
C5	0.622(2)	0.077(2)	0.322(1)	0.039(8)	C9	0.015(1)	0.215(1)	0.264(1)	0.017(6)
C6	0.679(2)	0.046(2)	0.360(2)	0.09(1)	C10	0.078(1)	0.228(1)	0.256(1)	0.025(7)
C7	0.632(2)	0.103(2)	0.275(1)	0.044(9)	C11	0.125(1)	0.260(1)	0.299(1)	0.024(7)
C8	0.580(1)	0.134(1)	0.238(1)	0.014(6)	C12	0.104(1)	0.282(1)	0.3441(9)	0.009(6)
C9	0.531(1)	0.342(2)	0.132(1)	0.033(8)	C13	0.154(1)	0.310(2)	0.389(1)	0.040(8)
C10	0.594(1)	0.304(2)	0.136(1)	0.035(8)	C14	0.043(1)	0.271(2)	0.349(1)	0.030(7)
C11	0.656(1)	0.342(2)	0.127(1)	0.028(8)	C15	-0.004(1)	0.234(2)	0.309(1)	0.027(7)
C12	0.650(1)	0.400(2)	0.116(1)	0.022(7)	C16	-0.132(1)	0.027(1)	0.062(1)	0.021(7)
C13	0.707(2)	0.438(2)	0.106(1)	0.041(8)	C17	-0.103(1)	-0.014(1)	0.028(1)	0.019(7)
C14	0.591(1)	0.447(2)	0.117(1)	0.036(8)	C18	-0.146(1)	-0.064(1)	-0.007(1)	0.026(7)
C15	0.533(1)	0.414(2)	0.121(1)	0.034(8)	C19	-0.206(1)	-0.073(1)	-0.002(1)	0.026(7)
C16	0.349(1)	0.114(1)	0.215(1)	0.018(7)	C20	-0.234(1)	-0.034(2)	0.028(1)	0.030(7)
C17	0.365(2)	0.044(2)	0.240(1)	0.039(9)	C21	-0.198(1)	0.020(2)	0.064(1)	0.037(8)
C18	0.325(1)	0.005(2)	0.265(1)	0.035(8)	C22	-0.061(1)	0.153(1)	0.0560(9)	0.015(6)
C19	0.261(1)	0.040(1)	0.264(1)	0.020(7)	C23	0.001(1)	0.167(1)	0.0476(9)	0.013(6)
C20	0.243(1)	0.104(2)	0.242(1)	0.029(8)	C24	0.011(1)	0.211(1)	0.009(1)	0.017(6)
C21	0.287(1)	0.140(2)	0.216(1)	0.026(7)	C25	-0.043(1)	0.247(2)	-0.025(1)	0.038(8)
C22	0.414(1)	0.087(1)	0.138(1)	0.021(7)	C28	-0.104(1)	0.238(2)	-0.013(1)	0.030(7)
C23	0.360(1)	0.043(1)	0.113(1)	0.023(7)	C27	-0.114(2)	0.100(2)	0.022(1)	0.037(8)
C24	0.366(2)	-0.004(2)	0.074(1)	0.037(8)	C28	-0.078(1)	0.283(1)	0.142(1) 0.1297(0)	0.022(7)
C25	0.426(1)	-0.017(2)	0.058(1)	0.038(8)	C30	-0.020(1)	0.230(1)	0.1207(9)	0.013(6)
C26	0.481(2)	0.026(2)	0.085(1)	0.06(1)	C31	-0.062(1)	0.347(1)	0.0942(9)	0.013(0) 0.023(7)
C27	0.474(2)	0.081(2)	0.122(1)	0.06(1)	C32	-0.119(1)	0.381(2)	0.073(1)	0.020(7)
C28	0.420(1)	0.226(2)	0.056(1)	0.025(7)	C33	-0.131(1)	0.325(1)	0.117(1)	0.021(7)
C29	0.366(2)	0.197(2)	0.021(1)	0.06(1)	C34	-0.155(1)	0.249(1)	0.213(1)	0.016(6)
C30	0.369(2)	0.153(2)	-0.020(2)	0.07(1)	C35	-0.218(1)	0.214(2)	0.211(1)	0.031(8)
C31	0.422(2)	0.141(2)	-0.034(2)	0.08(1)	C36	-0.259(2)	0.255(2)	0.235(1)	0.039(8)
C32	0.481(2)	0.162(2)	-0.001(1)	0.06(1)	C37	-0.240(2)	0.319(2)	0.261(1)	0.036(8)
C33	0.479(2)	0.209(2)	0.045(1)	0.00(1)	C38	-0.181(1)	0.347(1)	0.264(1)	0.020(7)
C24	0.337(1)	0.349(2) 0.354(2)	0.074(1)	0.029(7)	C39	-0.139(1)	0.309(2)	0.239(1)	0.031(8)
C35	0.293(1) 0.251(2)	0.334(2)	0.076(1)	0.039(8)	C40	-0.124(1)	0.078(2)	0.264(1)	0.025(7)
C30	0.231(2) 0.270(2)	0.403(2)	0.040(1)	0.051(9)	C41	-0.064(1)	0.049(1)	0.296(1)	0.024(7)
C38	0.275(2) 0.345(2)	0.430(2)	0.012(1)	0.00(1)	C42	-0.058(2)	-0.028(2)	0.317(1)	0.036(8)
C39	0.387(2)	0.307(2)	0.041(1)	0.050(1)	C43	- 0.046(2)	- 0.084(2)	0.278(1)	0.044(9)
C40	0.388(1)	0.396(2)	0.203(1)	0.028(7)	C44	-0.050(1)	-0.057(1)	0.223(1)	0.023(7)
C41	0.445(1)	0.418(1)	0.2312(9)	0.016(6)	C45	-0.106(1)	-0.035(2)	0.189(1)	0.036(8)
C42	0.461(1)	0.436(2)	0.289(1)	0.030(7)	C46	- 0.172(2)	- 0.032(2)	0.210(1)	0.040(8)
C43	0.453(1)	0.375(1)	0.326(1)	0.027(7)	C47	-0.184(1)	0.026(1)	0.244(1)	0.022(7)
C44	0.444(1)	0.299(1)	0.305(1)	0.026(7)	Minor o	lisorder atoms (s.o.f. = 0.057(3)		
C45	0.382(1)	0.279(2)	0.276(1)	0.035(8)	Ir2	0.548(2)	0.068(2)	0.291(2)	0.10(1)
C46	0.324(2)	0.323(2)	0.260(1)	0.047(9)	Ir3	0.952(2)	0.339(2)	0.219(2)	0.09(1)
C47	0.332(2)	0.387(2)	0.233(1)	0.043(9)	I4	0.422(3)	0.098(3)	0.234(2)	0.08(2)
					15	1.073(3)	0.307(3)	0.269(2)	0.08(2)

(continued)

^a $U_{eq} = 1/3$ of the trace of the orthogonalized U matrix. ^b Indicates major disorder atom (s.o.f. = 0.943(3)).

most stable metallacycles. Complexes containing a terdentate ligand that forms at least one four-membered metallacycle are relatively rare. They may, for example, be formed via cyclometallation of a bidentate ligand [30]. More than one four-membered metallacycle within one complex has, to our knowledge, only been found for tris(diphenylphosphino)methane in Fe(C₃H₅){CH-(PPh₂)₃] [31] or has been proposed as an intermediate, like in [M{CH(PPh₂)₃}(COD)] (M=Rh, Ir) [32] and our previous studies [9].

3.3. Reaction with MeOTf

Reaction of 1a or 1b with a stoichiometric amount of MeOTf yielded rapidly the complexes $[M(p-to-lyl-N=PPh_2-CH-PPh_2-NMe-p-tolyl)(COD)]OTf$ (5a or 5b, respectively) (Eq. (3)). In these reactions methylation of the nitrogen of the pendant iminophosphorane group of 1a or 1b has occurred.



In the ¹H NMR spectra of **5a** and **5b** the signal of the N-CH₃ group appears as a doublet at 2.58 and 2.67 ppm, respectively, with a ${}^{3}J(P,H)$ of ~9.5 Hz. The methanide hydrogen atom is found at 3.78 and 4.69 ppm for 5a and 5b, respectively. Both signals show a large coupling with the phosphorus nucleus of the pendant aminophosphonium group (15.2 and 17.4 Hz, respectively), whereas for 5a broadening of the signals is found due to unresolved coupling with the phosphorus of the coordinated iminophosphorane group and the rhodium nucleus. All values fall well within the range usually observed for iminophosphoranylmethanide [9,21] and aminophosphonium [10,33] compounds. For 5a, three signals are found for the olefinic COD protons at 3.75, 4.15 and 4.86 ppm (ratio 2:1:1). The observation of three signals, instead of the two which would be expected for a complex with C_s symmetry, is probably due to interaction of the OTf group with the Rh(I) atom. This is corroborated by the results of FD mass spectroscopy, in which a signal at m/z = 969 was found that can be attributed to [Rh(p-tolyl-N=PPh₂-CH-PPh₂-NMe-p-tolyl)OTf(COD)] (5a). In the ¹H NMR spectrum of 5b (M = Ir) two signals were observed for the olefinic COD protons, in line with C_s symmetry for this complex.

In the ³¹P NMR spectrum of **5a** and **5b**, the signal of the aminophosphonium group is found at 44.4 and 46.5 ppm, respectively. For **5a** broadening of the signal

occurs due to unresolved ${}^{2}J(P,P)$, whereas for 5b a ${}^{2}J(P,P)$ of 2.0 Hz is found. The resonances of the iminophosphoranylmethanide P atom are found at 19.7 and 34.7 ppm for 5a and 5b, respectively. Although these signals are found at somewhat lower frequencies than expected based on the chemical shift values of known complexes containing iminophosphoranylmethanide ligands [9b,21], they must be attributed to this group, since (i) a large high frequency shift is found in going from M=Rh to Ir, and (ii) in the spectrum of 5a a coupling of 19.7 Hz with the 103 Rh nucleus is found, which is a characteristic value for Rh(I)-iminophosphoranylmethanide complexes [9b,21].

When the reaction of 1a or 1b was performed with a fivefold excess of MeOTf in benzene, 5a or 5b was formed first, as could be inferred from in situ ³¹P NMR experiments. Subsequently a slow reaction took place and a brown oil had formed after one day. This reaction mixture contained, according to ¹H and ³¹P NMR, $[CH_2(PPh_2-NMe-p-tolyl)(PPh_2-NH-p-tolyl)]^{2+}$ and $[CH_2(PPh_2-NH-p-tolyl)_2]^{2+}$ [10]. Monitoring the reaction of 1b with MeOTf by using ³¹P NMR showed that during the reaction several products were formed, but after 4 days these were all converted into the aforementioned organophosphorus compounds. Most probably, apart from direct methylation of the N atom(s), also oxidative addition followed by subsequent elimination takes place. Subsequently, displacement of the ligand from the metal and/or hydrogen migration reactions occur, as evidenced by the product formation.

3.4. Reaction with MeI

Refluxing 1a or 1b with a tenfold excess of MeI in benzene for 3 h yielded exclusively $[MI(COD)]_2$ [12] and $[CH(PPh_2-NMe-p-tolyl)_2]^+I^-$ (6) (Eq. (4)).



The latter compound could unambiguously be identified by IR, ¹H, ¹³C and ³¹P NMR, FD mass spectroscopy and elemental analysis. An X-ray structure determination confirmed its structure [34]. [RhI(COD)]₂ and

 $[IrI(COD)]_2$ were identified by comparison with authentic samples, independently prepared from $[MCl(COD)]_2$ and NaI [12]. Interestingly, in the ¹H NMR spectrum of $[CH(PPh_2-NMe-p-tolyl)_2]^+I^-$ the N-CH₃ protons exhibit the coupling pattern of the X-part of an AA'X₃X'₃ spin system at 2.91 ppm, due to coupling with two magnetically inequivalent P nuclei. The methanide hydrogen atom appears as a triplet at 1.71 ppm (²J(P,H)=9.9 Hz).

Monitoring the thermal reaction between the Rh complex 1a and MeI by ³¹P NMR by taking samples of the reaction mixture every half hour showed that one other product accumulates: besides 1a and $[CH(PPh_2-NMe-p-tolyl)_2]^+I^-$ the mixture contained a product that showed a single resonance at 47.1 ppm (max. 5%). As the data point to two equivalent noncoordinating iminophosphorane moieties, this intermediate is most probably a Rh(I) coordination comthe type [RhI{CH(PPh2-NMe-p-topound of $lyl)_2(COD)^+I^-$ (7a). A similar compound 7b was observed in the reaction of 1b with MeI. Isolation of $[M(COD)I{CH(PPh_2-NMe-p-tolyl)_2}]^+I^-$ (7**a**,**b**) was successful due to their instability: not $[CH(PPh_2-NMe_p-tolyl)_2]^+I^-$, $[MI(COD)]_2$ and COD were obtained.

Besides these, two other compounds ($\sim 5\%$ each) were observed when monitoring the reaction of 1b with MeI by ³¹P NMR, which exhibit a pair of doublets at -7.1 and 52.1 ppm and -6.2 and 55.8 ppm, respectively, all signals showing ${}^{2}J(P,P)$ of 17.1 Hz. The proximity of these two pairs of signals indicates that two similar products are formed. The chemical shifts at lower frequencies (-7.1 and -6.2 ppm) are characteristic for uncoordinated iminophosphoranes [10,35], whereas those at 52.1 and 55.8 ppm are close to the value for the Ir(III)-bis(iminophosphoranyl)methanide complex 4. In view of additional correct mass spectroscopic data we feel confident that we are dealing with intermediates arising from oxidative addition of MeI, i.e. two isomeric (probably cis- and trans-) Ir(Me)(I){CH(PPh₂=N-ptolyl)₂}(COD) (8) complexes, in which the ligand is σ -N, σ -C chelating. Assuming other structures for 8, for instance terdentate coordination of the bis(iminophosphoranyl)methanide ligand with Me trans to the methanide C atom (an analogue of 4), is not in agreement with the spectroscopic data. Compound 8 does not convert into 7 upon adding MeI. Proposed structures for compounds 7 and 8 are given in Fig. 2.

4. Discussion

As addition of I_2 to the square planar Ir(I) complex 1b afforded exclusively the complex [IrI{CH(PPh₂=N-ptolyl)₂}(COD)]I (4), metal centred reactivity takes place in this case, which results in the oxidative addition of



Fig. 2. Proposed structures for 7 and 8 (M = Rh(a); Ir (b)).

diiodine. The unusual feature in this reaction is the fact that only one iodine atom coordinates to Ir(III), whereas the other occupies the second coordination sphere.

Several mechanisms have been put forward to account for the oxidative addition of halogens, i.e. radical [36], concerted addition [37] and polar (S_N2-type) reactions [6,7,38]. No evidence for the occurrence of iodine radicals in the reaction of 1b with I_2 was obtained. A concerted addition mechanism in which a side-on attack of I_2 is followed by insertion of the metal into the I-I bond would give excusively an oxidative addition product in which the iodine atoms end up in mutual cis positions. After initial addition of I_2 , one of the iodine ligands could then be substituted by coordination of the pendant iminophosphorane group of the terdentate ligand. In view of the severe mutual steric hindrance that would be exerted in the hypothetical diiodide complex cis- $[IrI_2{CH(PPh_2=N-p-tolyl)_2}(COD)]$, this alternative does not seem very likely. Although the possibility of a concerted addition followed by substitution of one iodide cannot be completely discarded, the fact that polar solvents like diethyl ether are needed and the notion that formation of 4 was faster in THF than in ether indicate that the reaction proceeds via a polar mechanism rather than a concerted mechanism. Hence the sequence of events can be represented as outlined in Scheme 1.

The first step ((i) in Scheme 1) is likely to be an end-on coordination of the iodine to the Ir(I) centre [6,7,38] by overlap of the filled d_{z^2} orbital on Ir with the empty σ^* orbital of the iodine molecule to give B. The occurrence of such intermediates has been substantiated by the isolation of a d⁸ (η^1 -I₂)Pt complex [6,7]. Oxidation of Ir(I) to Ir(III) occurs by an overall two-electron transfer from the metal to the coordinated I_2 , which may be accomplished via initial formation of the five-coordinate cation-anion intermediate of type C according to (ii) in Scheme 1, which reacts further to 4 by coordination of the second iminophosphorane moiety to the Ir centre according to (v). A rearrangement occurs in such a way that a structure is adopted in which the central methanide C atom is situated trans to I, being electronically most favourable due to the high trans influence of the hydrocarbyl group.

Apparently, the chelate effect of the tripodal bis(iminophosphoranyl)methanide ligand together with



Scheme 2.

the formation of the Ir-N bond is large enough to compensate for the alternative formation of a second Ir-I bond. Possibly, attack of a second iodide on the vacant sixth coordination site is furthermore inhibited by the steric bulk of the bis(iminophosphoranyl)methanide ligand.

Another reaction pathway could encompass electron transfer initiated by internal coordination of the pendant iminophosphorane group to the Ir centre to form **D** according to (iii) in Scheme 1. In the literature two organometallic compounds are known in which such a coordination of an (external) ligand precedes the formation of the oxidative addition complex [8,38]. Altogether the bis(iminophosphoranyl)methanide–Ir(III) complex 4 can be considered as a trapped cation–anion complex as a model for the situation halfway the polar oxidative addition of I_2 to a mononuclear 16-electron d⁸ transition metal fragment. In the present case, the reaction does not proceed beyond the stage of compound 4, which obtains its stability from the preference of N over I coordination to the d⁶ Ir centre and the resulting chelate effect.

The reaction of 1a or 1b with MeOTf is the result of direct nucleophilic attack of the nitrogen of the pendant iminophosphorane group on MeOTf, i.e. a ligand centred reactivity, similar to what has been found for reactions with CF₃COOH (Eq. (3)) [9]. This type of reactivity is in concert with the high Lewis acidity of the methyl group of MeOTf (as compared to MeI and I_2), hence its preference for direct interaction with the hard (pendant) nitrogen atom in 1a,b.

For the oxidative addition of MeI to metal complexes several competing mechanisms (i.e. nucleophilic attack, radical pathways) may be operating simultaneously [1,39]. A nucleophilic attack of the pendant iminophosphorane group on the methyl group (route (i)), Scheme 2), such as has been found for the reaction with MeOTf, is a viable route. As the stable N-methvlated complex 5 (see Eq. (3)), now with I^- as the anion) has not even been spectroscopically observed during this reaction, reaction with a second molecule of MeI must be faster than addition of the first. The formation of 8 indicates that oxidative addition may also occur first (according to (ii) in Scheme 2), followed by transfer of the methyl group from iridium to the coordinated N atom and reaction with a second molecule of MeI to give [IrI(COD]₂ and 6. As 8b is not converted into 7b, the latter must be formed via an independent pathway, probably by nucleophilic attack of an N atom on MeI (see above).

Although not observed, formation of 8a as an intermediate in the reaction of 1a with MeI is plausible in view of the identification of the related Ir compound 8b and leads in a straightforward way to the reaction products $[RhI(COD]_2$ and 6. The substantial contribution of the oxidative addition pathway ((ii) in Scheme 2) in the reaction of MeI, especially with Ir compound 1b, is in agreement with the less Lewis acidic (softer) character of MeI as compared to MeOTf (see above).

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References

- (a) R.H. Crabtree, Chem. Rev., (1985) 85, 245; (b) R.S. Dickson, Homogeneous Catalysis with Compounds of Rhodium and Iridium, Reidel, Dordrecht, Netherlands, 1985; (c) J.P. Collmann, L.S. Hegedus, J.R. Norton and R.G. Finke, Principles and Applications of Organotransition Metal Chemistry, University Science Books, Mill Valley, CA, 1987.
- [2] (a) D.N. Lawson, J.A. Osborn and G. Wilkinson, J. Chem. Soc.
 A, (1966) 1733; (b) P.G.H. Troughton and A.C. Skapski, J.
 Chem. Soc., Chem. Commun., (1968) 575.
- [3] R.H. Crabtree, J.W. Fuller, M.F. Mellea and J.M. Quirk, Organometallics, 1 (1982) 1361.
- [4] M.J. Burk, R.H. Crabtree and E.M. Holt, Organometallics, 3 (1984) 638.
- [5] M.J. Burk, B. Segmuller and R.H. Crabtree, Organometallics, 6 (1987) 2241.
- [6] J.A.M. van Beek, G. van Koten, W.J.J. Smeets and A.L. Spek, J. Am. Chem. Soc., 108 (1986) 5010.
- [7] (a) J. Terheijden, Ph.D. Thesis, University of Amsterdam, Netherlands, 1986; (b) J.A.M. van Beek, G. van Koten, G.P.C.M. Dekker, E. Wissing, M.C. Zoutberg and C.H. Stam, J. Organomet. Chem., 394 (1990) 659.
- [8] (a) A. Crispini, G. De Munno, M. Ghedini and F. Neve, *Inorg. Chem.*, 31 (1992) 4700; (b) R.J. Puddephatt and J.D. Scott, *Organometallics*, 4 (1985) 1221; (c) R. van Asselt, E. Rijnberg and C.J. Elsevier, *Organometallics*, 13 (1994) 706.
- [9] (a) P. Imhoff and C.J. Elsevier, J. Organomet. Chem., 361 (1989)
 C61; (b) P. Imhoff, R. van Asselt, J.M. Ernsting, C.J. Elsevier,
 K. Vrieze, W.J.J. Smeets, A.L. Spek and A.P.M. Kentgens,
 Organometallics, 12 (1993) 1523.
- [10] P. Imhoff, R. van Asselt, C.J. Elsevier, K. Vrieze, K. Goubitz, K.F. van Malssen and C.H. Stam, *Phosphorus Sulfur*, 47 (1990) 401.
- [11] D. Forster, J. Chem. Soc., Dalton Trans., (1979) 1639.
- [12] J. Chatt and L.M. Venanzi, J. Chem. Soc., (1957) 4735.
- [13] A.L. Spek, J. Appl. Crystallogr., 21 (1988) 578.
- [14] G.M. Sheldrick, SHELXS86, program for crystal structure determination, University of Göttingen, Germany, 1986.
- [15] P. van der Sluis and A.L. Spek, Acta Crystallogr., Sect. A, 46 (1990) 194.
- [16] D.T. Cromer and J.B. Mann, Acta Crystallogr., Sect. A, 24 (1968) 321.
- [17] D.T. Cromer and D. Liberman, J. Chem. Phys., 53 (1970) 1891.
- [18] G.M. Sheldrick, SHELX76, crystal structure analysis package, University of Cambridge, UK, 1976.
- [19] A.L. Spek, The EUCLID Package in Computational Crystallography, Clarendon, Oxford, 1982, p. 528.

- [20] (a) M. Hunziker, B. Hilti and G. Rihs, *Helv. Chim. Acta, 64* (1981) 82; (b) A. Millan, P.M. Bailey and P.M. Maitlis, *J. Chem. Soc., Dalton Trans.*, (1982) 73.
- [21] P. Imhoff, S.C.A. Nefkens, C.J. Elsevier, K. Goubitz and C.H. Stam, Organometallics, 10 (1991) 1421.
- [22] (a) K.V. Katti, U. Seseke and H.W. Roesky, *Inorg. Chem.*, 26 (1987) 814; (b) H. Schmidbaur and O. Gasser, *Angew. Chem.*, 88 (1976) 542.
- [23] H. Schmidbaur, O. Gasser, C. Krüger and C. Sekutowski, *Chem. Ber.*, 110 (1977) 3517.
- [24] (a) A. Davison and D.L. Reger, *Inorg. Chem.*, 10 (1971) 1967;
 (b) J. Browning, K.R. Dixon and R.W. Hilts, *Organometallics*, 8 (1989) 552.
- [25] J. Browning, K.A. Beveridge, G.W. Bushnell and K.R. Dixon, *Inorg. Chem.*, 25 (1986) 1987.
- [26] (a) J.S. Miller, M.O. Visscher and K.G. Caulton, Inorg. Chem., 13 (1974) 1632; (b) E.W. Abel and S.A. Mucklejohn, Z. Naturforsch., Teil B, 33 (1978) 339; (c) P. Dapporto, G. Denti, G. Dolcetti and M. Ghedini, J. Chem. Soc., Dalton Trans., (1983) 779; (d) K. Dehnicke and J. Strähle, Polyhedron, 8 (1989) 707; (e) P. Imhoff, C.J. Elsevier and C.H. Stam, Inorg. Chim. Acta, 175 (1990) 209.
- [27] (a) F.A. Cotton and R. Poli, Inorg. Chim. Acta, 122 (1986)
 243; (b) Organometallics, 6 (1987) 1743.
- [28] M.R. Churchill and S.A. Bezman, Inorg. Chem., 11 (1972) 2243.
- [29] M.R. Churchill and S.A. Julis, Inorg. Chem., 18 (1979) 1215.
- [30] T. Ikariya and A. Yamamoto, J. Organomet. Chem., 118 (1976) 65.
- [31] J.D. Goodrich and J.P. Selegue, Organometallics, 4 (1985) 798.
- [32] H. El-Amouri, A.A. Bahsoun and J.A. Osborn, *Polyhedron*, 7 (1988) 2035.
- [33] (a) W. McFarlane, Proc. R. Soc. London, Ser. A, 306 (1968) 185; (b) D.G. Gorenstein, Prog. Nucl. Magn. Reson. Spectrosc., 16 (1983) 1; (c) L.K. Krannich, R.K. Kanjolia and C.L. Watkins, Magn. Reson. Chem., 25 (1987) 320.
- [34] A.L. Spek, W.J.J. Smeets, P. Imhoff and C.J. Elsevier, to be published.
- [35] M. Pomerantz, D.S. Marynick, K. Rajeshwar, W.N. Chou, L. Throckmorton, E.W. Tsai, P.C.Y. Chen and T. Cain, J. Org. Chem., 51 (1986) 1223.
- [36] D. Hopgood and R.A. Jenkins, J. Am. Chem. Soc., 95 (1973) 4461.
- [37] (a) L.M. Haines, *Inorg. Chem.*, 10 (1971) 1693; (b) G.J. van Zijl, G.J. Lamprecht and J.G. Leipoldt, *Inorg. Chim. Acta*, 129 (1987) 35.
- [38] (a) M.M. Jones and K.A. Morgan, *Inorg. Nucl. Chem.*, 34 (1972) 259; (b) K.A. Morgan and M.M. Jones, *Inorg. Nucl. Chem.*, 34 (1972) 275; (c) S.S.M. Ling, N.C. Payne and R.J. Puddephatt, *Organometallics*, 4 (1985) 1546; (d) S.P. Schmidt, W.C. Trogler and F. Basalo, J. Am. Chem. Soc., 106 (1984) 1308.
- [39] (a) L.H. Hall, M.F. Lappert and P.W. Lednor, J. Chem. Soc., Dalton Trans., (1980) 1448; (b) G. Ferguson, P.K. Monaghan, M. Parvez and R.J. Puddephatt, Organometallics, 4 (1985) 1669; (c) R.H. Hill and R.J. Puddephatt, J. Am. Chem. Soc., 107 (1985) 1218; (d) A.J. Pearson, Metallo-organic Chemistry, Wiley, Chichester, UK, 1985.