

Straightforward synthesis of phosphametalloccenium cations of Rh and Ir

Verena Schnitzler, Walter Frank, Christian Ganter*

Institut für Anorganische Chemie und Strukturchemie, Heinrich-Heine-Universität Düsseldorf, Universitätsstr. 1, 40225 Düsseldorf, Germany

ARTICLE INFO

Article history:

Received 26 March 2008

Received in revised form 24 April 2008

Accepted 28 April 2008

Available online 6 May 2008

Keywords:

Phosphametalloccenes

Rhodium

Iridium

Phosphole

ABSTRACT

Reaction of 3,4-dimethylphospholythallium (Tl-1) with $[\text{Cp}^*\text{MCl}_2]_2$ ($\text{M} = \text{Rh}, \text{Ir}$) leads to the formation of the dimeric species $[(\text{Cp}^*\text{M})_2(\text{Me}_2\text{C}_4\text{H}_2\text{P})_3]^+$ **2** and **3** with bridging $\mu\text{-}\eta^1\text{:}\eta^1\text{-phospholyl}$ ligands. The phosphametalloccenium sandwich complexes $[\text{Cp}^*\text{M}(\text{Me}_2\text{C}_4(\text{SiMe}_3)_2\text{P})]^+$ **7** ($\text{M} = \text{Rh}$) and **8** ($\text{M} = \text{Ir}$) could be obtained from the reaction of $[\text{Cp}^*\text{MCl}_2]_2$ and the 2,5-bis(trimethylsilyl)-1-trimethylstannylphosphole **6**, with the bulky trimethylsilyl groups preventing the phosphole from $\eta^1\text{-}$ and enforcing a $\eta^5\text{-}$ coordination. The structures of phospharhodocenium cation **7** and a byproduct **9** containing a phosphairidocenium moiety could be determined by X-ray diffraction.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Since the discovery of the first phosphaferrrocene by Mathey [1] in 1977, phosphametalloccenes in general have been thoroughly investigated. However, the greatest wealth of results was obtained with phosphaferrrocenes [2], including – among others – applications as chiral ligands in homogeneous catalysis [3]. Phosphametalloccenes of other central metals have received less attention. Synthetic protocols for the preparation of phosphaferrrocenes with a great variety of substitution patterns and functional groups are available, which cannot be extended to the synthesis of phosphametalloccenes with other metals in many cases. For example, the limitations are due to redox processes when phospholide anions of electropositive metals are employed which frequently reduce noble metal salts to the elemental form. Other problems may arise from the different coordination modes phospholyl ligands can adopt: instead of forming the desired $\eta^5\text{-}$ complexes, the formation of complexes with $\eta^1\text{-P}$ coordination is frequently observed leading to dimeric species featuring the phospholyl system in a $\mu\text{-}\eta^1\text{:}\eta^1\text{-P}$ bridging mode. Strategies to overcome these problems include the use of more covalently bound phospholyl transfer reagents with p-block elements, which have drastically diminished reducing power and steric protection by incorporating sterically demanding groups in 2- and 5-position of the phospholyl ring, thus preventing $\eta^1\text{-P}$ and enforcing a $\eta^5\text{-}$ coordination. In that context, the 2,5-di(*t*-butyl)phospholyl unit has proven to be of high synthetic value. The lithium salt [4] allowed the preparation of sandwich compounds with Ru [4], Co [5] and Ni [6], while the more covalent and less reducing 2,2',5,5'-tetrakis(*t*-butyl)diphospha-

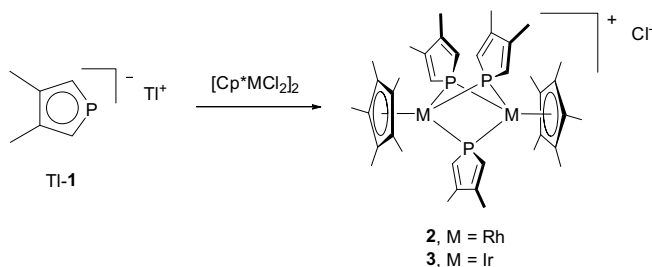
plumbocene [7] was successfully employed to obtain phosphametalloccenes with Co [8,9] Rh [8] and Ir [8]. Nonamethylphospharhodocenium and -iridocenium cations were also prepared by the nucleophilic degradation of the respective triple-decker complexes $[\text{Cp}^*\text{M-}\mu\text{-}\eta^5\text{:}\eta^5\text{-PC}_4\text{Me}_4\text{-FeCp}^*]^{2+}$ in acetone [10]. As ligands to transition metal fragments, phosphaferrrocenes as well as the homologous phospharuthenocenes are considered to be quite poor $\sigma\text{-}$ donors with considerable $\pi\text{-}$ acceptor character, thus resembling phosphites $\text{P}(\text{OR})_3$ much more closely than the ubiquitous phosphines PR_3 [2a]. Within a research program aimed at the tuning of the donor/acceptor characteristics of phosphametalloccenes, we became interested in cationic phosphametalloccene derivatives as these might behave as even stronger acceptor ligands when coordinated to metal fragments. In this contribution, we describe the preparation of cationic phospharhodocenium and iridocenium complexes with the sterically demanding 2,5-bis(trimethylsilyl)-3,4-dimethylphospholyl ligand.

2. Results and discussion

First synthetic attempts were made using 3,4-dimethylphospholythallium (Tl-1), which was obtained following the procedure described by Nief for the parent thalliumphospholide without methyl substituents [11]. Addition of TIOEt to a THF solution of 3,4-dimethylphospholide as its Li salt (Li-1) caused the immediate precipitation of the Tl-1 as a pale yellow solid in 82% yield, which was purified by sublimation in high vacuum. While in a test reaction treatment of Tl-1 with $(\text{CO})_5\text{MnBr}$ gave a 67% yield of the desired $\eta^5\text{-}$ complex 3,4-dimethylphosphacymanthrene, the reaction with the dimeric complexes $[\text{Cp}^*\text{MCl}_2]_2$ ($\text{M} = \text{Rh}, \text{Ir}$) gave not the phosphametalloccenium complexes, but instead lead to the formation of the dimeric species **2** and **3**, whose structures were deduced

* Corresponding author.

E-mail address: christian.ganter@uni-duesseldorf.de (C. Ganter).

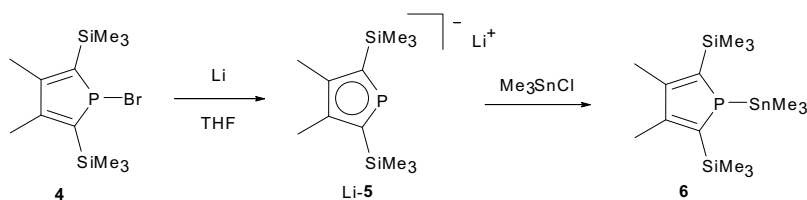


Scheme 1.

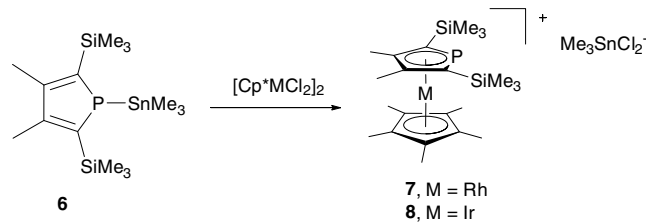
from the spectroscopic and analytical data (Scheme 1). The outcome of this reaction was not completely unexpected, as related dimeric complexes with ruthenium [12] and nickel [13] with bridging phospholyl ligands have been described before. The mass spectra (MALDI and FAB) of complexes **2** and **3** feature molecular ion peaks for the cationic $[(Cp^*M)_2(Me_2C_4H_2P)_3]^+$ fragments, the ^{31}P NMR resonances at -86.5 (Rh) and -166.2 ppm (Ir) are in the range expected for bridging phospholes and the resonance of the Rh complex appears as a triplet with $^1J_{P-Rh} = 84$ Hz due to the coupling with the two Rh atoms. In the related bis-phosphido bridged complex $[Cp^*RhCl(\mu-PMe_2)]_2$ a coupling constant of $^1J_{P-Rh} = 95.3$ Hz was observed [14].

Obviously, steric protection of the phosphole was mandatory in order to achieve the desired η^5 -coordination. However, as we were interested to test the phosphametalocenium complexes for their potential towards metal coordination, we decided not to use the 2,5-di(*t*butyl)phospholyl ligand but the related 2,5-bis(trimethylsilyl)-3,4-dimethylphospholyl system **5** (Scheme 2). This ligand provides suitable steric protection to achieve the desired coordination mode but once the η^5 complex has been formed the Me_3Si groups may hopefully be removed and replaced by a proton in order to reduce the steric congestion around the P atom and thus to allow for the η^1 coordination of an additional metal fragment to the P atom. Furthermore, the Me_3Si group could also be converted into another functional group such as trifluoroacetyl [12] which can be subsequently converted into a donor function, thus leading to a potentially bidentate ligand. Thus the anion **5** was prepared according to the literature via the Cp_2Zr -mediated coupling of trimethylsilylpropyne, treatment of the zirconacycle with PBr_3 and cleaving the P–Br bond of the bromophosphole **4** by elemental lithium [15].

The formation of the phospholide anion **5** can easily be monitored by ^{31}P NMR spectroscopy [δ (**4**) = 78 ppm, δ (**5**) = 141 ppm]. As stannylphospholes have proven to be valuable phospholyl transfer reagents without causing redox problems [16], we turned our attention to the trimethylstannyl derivative **6** which could be obtained as a pale yellow solid in 91% yield by treatment of the lithium phospholide **5** with Me_3SnCl (Scheme 2). The P–Sn linkage is apparent from the ^{31}P NMR spectrum which shows a signal at -15.2 ppm with tin satellites due to the 1J coupling with the isotopes ^{117}Sn (591 Hz) and ^{119}Sn (566 Hz) in almost equal intensities as expected from their natural abundances. Accordingly, the ^{119}Sn



Scheme 2.



Scheme 3.

NMR spectrum features a doublet at 18.3 ppm with $^1J(P-Sn) = 594$ Hz. Both values are comparable to those observed for other stannyl phospholes [16]. Interestingly, attempts to convert the phospholide **5** into the corresponding phosphaplumbocene derivative by treatment with $PbCl_2$ was not successful leading to a non isolable species, which decomposed quite rapidly.

Finally, reaction of the tin compound **6** with the dimeric Rh and Ir complexes $[Cp^*MCl_2]_2$ in dichloromethane at low temperature proceeded smoothly to give the desired cationic η^5 -phospholyl complexes **7** (M = Rh, 84%) and **8** (M = Ir, 75%), respectively (Scheme 3). The ^{31}P NMR spectra show resonances at 58.5 (**7**) and 19.5 ppm (**8**) which are shifted considerably towards lower field as compared to the analogous di-*t*butyl [**8**] and tetramethyl [**10**] complexes. The value of the coupling constant $^1J(P-Rh) = 24$ Hz is in the same range as for the other two examples mentioned. Recrystallisation from acetone and diethylether furnished crystals of **7** as the $Me_3SnCl_2^-$ salt suitable for X-ray diffraction. If the crude product is purified by column chromatography on silica, Me_3SnCl can be first eluted with dichloromethane where after **7**-Cl is eluted with dichloromethane/methanol (10:1). The cation **7** features the typical characteristics of a sandwich type structure with almost coplanar η^5 -coordinated rings (Fig. 1). The deviation of the phospholyl ring from planarity is small (max. deviation from mean plane: 0.014 Å for C1; angle between mean planes through C1, C2, C3, C4 and C1, P, C4: 2.0°), as is the angle between the least-squares planes for the C_5P and the Cp^*-C_5 (2.8°). The distances of the ring centroids ct1 and ct2 from Rh are almost identical (1.8144 Å (ct1), 1.8116 Å (ct2)). The most severe deviations from ideality concern the bulky Me_3Si groups: due to their steric interference with the C_5Me_3 ring, the vectors C1–Si2 and C4–Si1 are tilted out of the phospholyl ring plane away from the Rh atom by 5.6° (Si1) and 6.7° (Si2), respectively. Overall, the observed geometrical parameters are close to the respective values observed for related structures, for example $[Cp^*M(2,5-tBu_2C_4H_2P)]BPh_4$ (M = Co, Rh) [**8**], $[Cp^*Ru(2,5-tBu_2C_4H_2P)]$ [**4**] and $[Cp^*Fe-5]$ [**15a**]. While the deviations for the structures with Rh and Ru are very small, the sandwich complexes for the first row elements Fe and Co feature significantly shorter M-centroid distances leading to bigger tilt angles for the ring C–SiMe₃ (Co: 10.6°) and C–*t*Bu (Fe: 9.9°) vectors.

Interestingly, attempts to obtain crystals of the Ir complex **8** from dichloromethane/ether failed and instead a byproduct **9** crystallized, whose formation is unclear. The amount of this byproduct is small, as there were no signals observed for it in the NMR spectra of the crude product. However, we suppose that the byproduct is

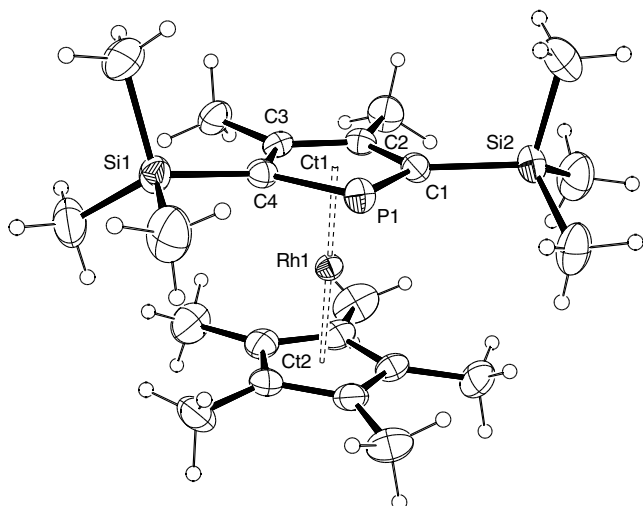


Fig. 1. Molecular structure of cation **7** in the solid state. The $\text{Me}_3\text{SnCl}_2^-$ anion is omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): Rh(1)–P(1) 2.3845(9), Rh(1)–C(1) 2.226(4), Rh(1)–C(2) 2.199(3), Rh(1)–C(3) 2.198(3), Rh(1)–C(4) 2.229(3), P(1)–C(1) 1.776(4), P(1)–C(4) 1.777(4), Si(1)–C(4) 1.877(3), Si(2)–C(1) 1.896(4), C(1)–C(2) 1.410(5), C(2)–C(3) 1.424(5), C(3)–C(4) 1.428(5); C(1)–P(1)–C(4) 91.81(16), C(2)–C(1)–P(1) 110.8(3), C(2)–C(1)–Si(2) 128.1(3), P(1)–C(1)–Si(2) 120.21(19), C(1)–C(2)–C(3) 113.8(3), C(1)–C(2)–C(5) 123.9(3), C(3)–C(2)–C(5) 122.2(3), C(2)–C(3)–C(4) 112.9(3), C(3)–C(4)–P(1) 110.5(2), C(3)–C(4)–Si(1) 130.0(3), P(1)–C(4)–Si(1) 118.91(19).

formed during the reaction, because attempts to convert the phosphairidocenium complex **8** into **9** were unsuccessful. The molecular structure of complex **9** is depicted in Fig. 2 together with selected geometrical data.

The structure consists of two subunits, a phosphairidocenium sandwich unit and a Cp^*IrCl_2 half-sandwich unit. The Ir coordination

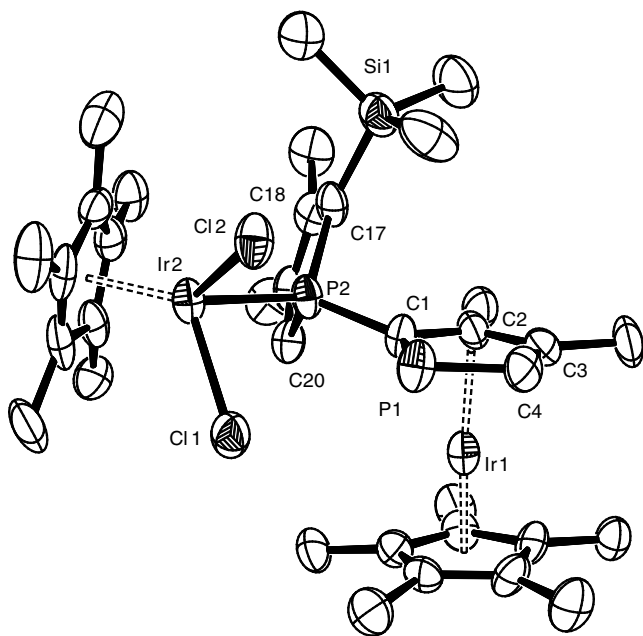
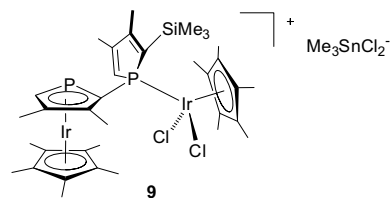


Fig. 2. Molecular structure of cation **9** in the solid state. The $\text{Me}_3\text{SnCl}_2^-$ anion, all H-atoms and the solvating ether molecule are omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): Ir(1)–C(2) 2.190(13), Ir(1)–C(4) 2.192(13), Ir(1)–C(3) 2.212(13), Ir(1)–C(1) 2.221(14), Ir(1)–P(1) 2.408(4), Ir(2)–P(2) 2.334(3), P(2)–Cl(1) 2.368(4), Ir(2)–Cl(2) 2.418(4), P(1)–C(4) 1.762(15), P(1)–C(1) 1.789(14), P(2)–C(20) 1.798(15), P(2)–C(17) 1.818(14), P(2)–C(1) 1.842(13), C(1)–C(2) 1.451(17), C(2)–C(3) 1.43(2), C(3)–C(4) 1.40(2), C(17)–C(18) 1.37(2), C(18)–C(19) 1.49(2), C(19)–C(20) 1.33(2); C(4)–P(1)–C(1) 87.7(7), C(20)–P(2)–C(17) 93.7(7), C(1)–P(2)–Ir(2) 119.2(4), P(2)–Ir(2)–Cl(1) 85.40(13), P(2)–Ir(2)–Cl(2) 92.16(12), Cl(1)–Ir(2)–Cl(2) 90.98(17).



Scheme 4.

tion sphere of the latter is completed by P-coordination of a bridging phosphole, which is also P-bound to the α -carbon atom of the η^5 -phospholyl ring (Scheme 4). To the best of our knowledge, compound **9** is the first example of a structurally characterized η^5 -phospholyl iridium complex. The structural features of the phosphairidocenium unit resemble those of the phospharhodoocenium complex **7** very closely: the distances of the Ir atom to the centroids of the phospholyl (1.8104 Å) and Cp^+ rings (1.8085 Å), the distances and angles within the phospholyl ring and the deviation of the two η^5 rings from coplanarity (175.5°) are almost identical to the related values in complex **7**. The most pronounced deviation from ideality again concerns the arrangement of the exocyclic C1–P2 bond, which forms an angle of 11.1° with the C_4P plane. The phosphole ring containing P2 shows the typical bond localization with long P–C and C18–C19 bonds while the formal double bonds (C17–C18 and C19–C20) are short. In contrast, the bond lengths equilibration in the phospholyl ring around P1 reflects its aromatic character. For the Cp^*Ir half-sandwich unit, the distance centroid(Cp^*)–Ir2 (1.8253 Å) is again almost identical to the related distance within the phosphairidocenium unit.

First attempts to remove the Me_3Si groups in the α -positions turned out to be difficult and resulted in product mixtures. We are working on that problem currently in our laboratory.

3. Experimental

3.1. General

All reactions were carried out under an atmosphere of dry nitrogen by means of conventional Schlenk techniques. Solvents were dried and purified by standard methods. Alumina was heated at 200°C for 12 h, cooled to room temperature under high vacuum, deactivated with 5% water and stored under nitrogen. NMR spectra were recorded on a Bruker Avance DRX 500 and a Bruker Avance DRX 200 spectrometer. ^1H and $^{13}\text{C}\{^1\text{H}\}$ spectra are referenced to the residual solvent signal and $^{31}\text{P}\{^1\text{H}\}$ spectra to external H_3PO_4 (85%). Mass spectra were recorded on a Finnigan MAT 8200 (FAB, EI). Elemental analyses were performed by the Institute of Pharmaceutical Chemistry at the Heinrich-Heine-Universität Düsseldorf on a Perkin-Elmer elemental analyser 2400 Series II CHN. 3,4-Dimethyl-1-phenylphosphole [17] and 2,5-bis(trimethylsilyl)-3,4-dimethyl-1-bromophosphole **4** [15f] were prepared according to published procedures.

3.2. Synthesis of thallium-3,4-dimethylphospholide (Tl-1)

To a solution of 3,4-dimethyl-1-phenylphosphole (1.09 g, 5.47 mmol) in 50 mL THF lithium pieces were added in excess. After 3 h at room temperature the reduction of the phosphole is completed. The excess lithium was removed and *tert*-butylchloride (0.63 mL, 5.74 mmol) was added. The reaction mixture was heated to reflux for 15 min and then cooled down to -35°C . Thalliumethanolate (0.39 mL, 5.5 mmol) was added dropwise by syringe and a yellow solid precipitated which was separated by filtration, washed with acetone and dried under high vacuum. The crude

product was obtained in yields of 82% and it was purified by sublimation. ^1H NMR (200 MHz, DMSO- d_6): δ = 2.20 (s, 6H, CH_3), 6.31 (d, $^2J_{\text{P-H}}$ = 39.1 Hz, 2H, $\text{C}_\alpha\text{-H}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (81 MHz, DMSO): δ = 54.2 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, DMSO- d_6): δ = 16.7 (s, CH_3), 130.2 (d, $^1J_{\text{P-C}}$ = 41.2 Hz, C_α), 134.9 (d, $^2J_{\text{P-C}}$ = 5.5 Hz, C_β). MS (EI, 70 eV): m/z (fragment, I_{rel}) = 316 (M^+ , 28%); 205/203 (Ti^+ , 100%/45%). Anal. Calc. for $\text{C}_6\text{H}_8\text{PTI}$: C, 22.84; H, 2.56. Found: C, 22.87; H, 2.31%.

3.3. Synthesis of $[(\mu^2\text{-3,4-dimethylphospholy})_3(\text{Ircp}^*)_2]^+\text{Cl}^-$ (**3**)

A mixture of **Tl-1** (0.36 g, 1.15 mmol) and $[\text{Cp}^*\text{Ir}^+\text{Cl}_2]_2$ (0.43 g, 0.55 mmol) in 50 mL THF was refluxed for 1 h. The beige solid was removed by filtration (Celite) and washed with THF until the washing solution was colorless. The solvent was removed under high vacuum and the crude product was purified by chromatography on alumina with methanol. Compound **3** was obtained as a yellow solid after removal of solvent in vacuum. (0.35 g, 30%). ^1H NMR (200 MHz, CDCl_3): δ = 1.52 (q, $^4J_{\text{P-H}}$ = 1.8 Hz, 30H, cp^*), 2.35 (s (br), 18H, $\text{C}_\beta\text{-CH}_3$), 6.15–6.36 (m, 6H, $\text{C}_\alpha\text{-H}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (81 MHz, CDCl_3): δ = -166.2 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3): δ = 8.6 (s, $\text{Cp}^*\text{-CH}_3$), 17.3 (m, $\text{C}_\beta\text{-CH}_3$), 94.5 (s, $\text{cp}^*\text{-C}$), 122.5 (s (br), C_α), 151.4 (m, $\text{C}_\beta\text{-CH}_3$). MS (MALDI): m/z (fragment, I_{rel}): 988 ($(\text{M}-\text{Cl})^+$, 100%). Anal. Calc. for $\text{C}_{38}\text{H}_{54}\text{P}_3\text{Ir}_2\text{Cl}_2$: C, 44.59; H, 5.32. Found: C, 42.04; H, 5.07%.

3.4. $[(\mu^2\text{-3,4-Dimethylphospholy})_3(\text{Rhcp}^*)_2]^+\text{Cl}^-$ (**2**)

Prepared as described above for **3**. ^1H NMR (200 MHz, CDCl_3): δ = 1.41 (q, $^4J_{\text{P-H}}$ = 2.5 Hz, 30H, cp^*), 2.61 (s (br), 18H, $\text{C}_\beta\text{-CH}_3$), 6.25–6.5 (m, 6H, $\text{C}_\alpha\text{-H}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (81 MHz, CDCl_3): δ = -86.5 (t, $^1J_{\text{Rh-P}}$ = 84.4 Hz). MS, m/z (fragment, I_{rel}), FAB: 809 ($(\text{M}-\text{Cl})^+$, 75%); MALDI: 809 ($(\text{M}-\text{Cl})^+$, 69%).

3.5. Synthesis of 2,5-bis(trimethylsilyl)-3,4-dimethyl-1-(trimethylstannyl)-phosphole (**6**)

To a solution of 2,5-bis(trimethylsilyl)-1-bromo-3,4-dimethylphosphole (**4**) (0.263 g, 0.74 mmol) in 15 mL THF was added an excess of elemental lithium and the mixture was stirred for 4 h at room temperature when the reduction of the phosphole was completed. The excess lithium was removed, 150 mg of trimethyltinchloride was added and the mixture was stirred for half an hour at room temperature. The solvent was removed under high vacuum and the crude product was taken up in hexane (ultrasound sonication) and the solid was removed by filtration over celite. The hexane was removed under high vacuum to give a pale yellow solid (290 mg, 91%). ^1H NMR (200 MHz, CDCl_3): δ = 0.09 (d, $^4J_{\text{P-H}}$ = 1.5 Hz, $^2J_{\text{Sn-H}}$ = 49.4/52.0 Hz, 9H, Sn-CH_3), 0.29 (d, $^4J_{\text{P-H}}$ = 0.8 Hz, $^5J_{\text{Sn-H}}$ = 5.5/7.3 Hz, 18H, Si-CH_3), 2.30 (d, $^4J_{\text{P-H}}$ = 1.3 Hz, $^5J_{\text{Sn-H}}$ = 17.1/19.6 Hz, 6H (C-CH_3)). $^{31}\text{P}\{^1\text{H}\}$ NMR (81 MHz, CDCl_3): δ = -15.2 (s, $^1J_{\text{P-Sn}}$ = 591 Hz (^{119}Sn), 566 Hz (^{117}Sn)). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3): δ = -6.2 (d, $^2J_{\text{P-C}}$ = 4.6 Hz, $^1J_{\text{Sn-C}}$ = 296/310 Hz, Sn-CH_3), 0.7 (d, $^3J_{\text{P-C}}$ = 4.6 Hz, Si-CH_3), 18.1 (d, $^2J_{\text{P-C}}$ = 4.6 Hz C-CH_3), 145.2 (d, $^1J_{\text{P-C}}$ = 44.0 Hz, C_α), 157.0 (d, $^2J_{\text{P-C}}$ = 2.7 Hz, $\text{C}_\beta\text{-CH}_3$). $^{119}\text{Sn}\{^1\text{H}\}$ NMR (186 MHz, CDCl_3): δ = 18.3 (d, $^1J_{\text{P-Sn}}$ = 594 Hz). MS (EI, 70 eV): m/z (fragment, I_{rel}) = 147 (SnC_2H_3 , 100%), 149 (SnC_2H_5 , 82%), 165 (SnC_3H_9 , 68%).

3.6. Synthesis of 2,5-bis(trimethylsilyl)-3,4-dimethylphospholy-pentamethyl-cyclopentadienylrhodocenium/iridocenium cations (**7/8**)

To a solution of trimethyltinphosphole **6** (Rh: 268 mg, 0.62 mmol; Ir: 141 mg, 0.33 mmol) in 12 mL CH_2Cl_2 at -78°C was added slowly a solution of $[\text{Cp}^*\text{RhCl}_2]_2$ (194 mg, 0.31 mmol)/ $[\text{Cp}^*\text{IrCl}_2]_2$ (127 mg, 0.16 mmol) in 15/10 mL CH_2Cl_2 . The mixture

was stirred for 10 min at -78°C and then allowed to warm to room temperature while stirring was continued for 4 h. The solvent was removed in high vacuum and the crude product was purified by chromatography on silica. Byproducts were first eluted with CH_2Cl_2 and the product was obtained with $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ (10:1). Removal of solvents yielded the chloride salts **7-Cl** (275 mg, 84%) and **8-Cl** (152 mg, 75%) as orange powders.

Alternatively, cation **7** can also be isolated as $\text{Me}_3\text{SnCl}_2^-$ -salt from the crude product prior to chromatography by precipitation from acetone solution with ether. **7-Me}_3\text{SnCl}_2 was obtained as an orange powder (298 mg, 66%).**

3.7. **7** [Me_3SnCl_2]

^1H NMR (200 MHz, CDCl_3): δ = 0.31 (d, $^4J_{\text{P-H}}$ = 1 Hz, 18H, Si-CH_3), 0.79 (s, $^2J_{\text{Sn-H}}$ = 65.0/68.0 Hz, 9H, Sn-CH_3), 2.07 (s, 15H, $\text{Cp}^*\text{-CH}_3$), 2.11 (s, 6H, $\text{C}_\beta\text{-CH}_3$). $^{31}\text{P}\{^1\text{H}\}$ NMR (81 MHz, CDCl_3): δ = 59.5 (d, $^1J_{\text{Rh-P}}$ = 24.0 Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3): δ = 0.8 (d, $^3J_{\text{P-C}}$ = 5.5 Hz, Si-CH_3), 5.9 (s, $^1J_{\text{Sn-C}}$ = 486/509 Hz, Sn-CH_3), 10.9 (s, CH_3 der cp^*), 13.4 (s, $\text{C}_\beta\text{-CH}_3$), 102.9 (d, $^1J_{\text{Rh-C}}$ = 7.3 Hz, C-CH_3 der cp^*), 114.6 (dd, $^1J_{\text{P-C}}$ = 85.2 Hz, $^1J_{\text{Rh-C}}$ = 8.2 Hz, C_α), 118.8 (t, $^2J_{\text{P-C}}$ = $^1J_{\text{Rh-C}}$ = 5 Hz, C_β). Anal. Calc. for $\text{C}_{25}\text{H}_{48}\text{PSi}_2\text{-RhSnCl}_2$: C, 41.23; H, 6.64. Found: C, 41.46; H, 6.69%.

3.8. **7 Cl**

^1H NMR (200 MHz, CDCl_3): δ = 0.33 (d, $^4J_{\text{P-H}}$ = 1.0 Hz, 18H, Si-CH_3), 2.13 (s, 15H, $\text{Cp}^*\text{-CH}_3$), 2.19 (s, 6H, $\text{C}_\beta\text{-CH}_3$). $^{31}\text{P}\{^1\text{H}\}$ NMR (81 MHz, CDCl_3): δ = 58.5 (d, $^1J_{\text{Rh-P}}$ = 24.0 Hz). MS (FAB): m/z (fragment, I_{rel}) = 493 (7^+ , 100%).

3.9. **8 Cl**

^1H NMR (200 MHz, CDCl_3): δ = 0.30 (d, $^4J_{\text{P-H}}$ = 1.0 Hz, 18H, Si-CH_3), 2.17 (s, 6H, $\text{C}_\beta\text{-CH}_3$), 2.18 (s, 6H, $\text{Cp}^*\text{-CH}_3$). $^{31}\text{P}\{^1\text{H}\}$ NMR (81 MHz, CDCl_3): δ = 19.5 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3): δ = 0.7 (d, $^3J_{\text{P-C}}$ = 5.5 Hz, Si-CH_3), 10.6 (s, $\text{Cp}^*\text{-CH}_3$), 12.9 (s, $\text{C}_\beta\text{-CH}_3$), 96.8 (s, $\text{Cp}^*\text{-C-CH}_3$), 102.1 (d, $^1J_{\text{P-C}}$ = 84.3 Hz, C_α), 111.6 (d, $^2J_{\text{P-C}}$ = 5.5 Hz, C_β). MS (FAB): m/z (fragment, I_{rel}) = 583 (8^+ , 100%).

3.10. Crystal data for **7** [Me_3SnCl_2]

$\text{C}_{25}\text{H}_{48}\text{Cl}_2\text{PRhSi}_2\text{Sn}$, $M = 728.30$ g/mol, orthorhombic, $Pbca$, $a = 14.6643(10)$ Å, $b = 20.1655(11)$ Å, $c = 22.8381(13)$ Å, $V = 6753.5(7)$ Å³, $Z = 8$, D (calcd) = 1.433 Mg/m³, $\mu = 1.517$ mm⁻¹, $F(000) = 2960$, crystal size $0.60 \times 0.58 \times 0.18$ mm³, $T = 293$ K, Mo $K\alpha$ ($\lambda = 0.71073$ Å), $1.93^\circ < \theta < 25.00^\circ$, total of 84249 reflections, 5939 independent reflections [$R(\text{int}) = 0.1037$], completeness to $\theta = 25.00^\circ$: 99.9%, full-matrix least-squares refinement on F^2 , 5939 data, 305 parameters, goodness-of-fit on $F^2 = 1.007$, $R_1 = 0.037$, $wR_2 = 0.091$ [$I > 2\sigma(I)$], $R_1 = 0.045$, $wR_2 = 0.092$ (all data). Largest difference peak and hole: 1.22/-0.94 e Å⁻³ (near Rh).

3.11. Crystal data for **9** [Me_3SnCl_2] · Et_2O

$\text{C}_{42}\text{H}_{72}\text{Cl}_4\text{Ir}_2\text{OP}_2\text{Si}_2\text{Sn}$, $M = 1327.92$ g/mol, triclinic, $P\bar{1}$, $a = 11.5275(8)$ Å, $b = 13.4145(10)$ Å, $c = 16.3871(13)$ Å, $\alpha = 96.883(10)^\circ$, $\beta = 90.278(9)^\circ$, $\gamma = 90.607(9)^\circ$, $V = 2515.6(3)$ Å³, $Z = 2$, D (calcd) = 1.753 Mg/m³, $\mu = 6.099$ mm⁻¹, $F(000) = 1296$, crystal size $0.35 \times 0.20 \times 0.05$ mm³, $T = 291$ K, Mo $K\alpha$ ($\lambda = 0.71073$ Å), $1.86^\circ < \theta < 25.00^\circ$, total of 33067 reflections, 8344 independent reflections [$R(\text{int}) = 0.131$], completeness to $\theta = 25.00^\circ$: 94.2%, full-matrix least-squares refinement on F^2 , 8344 data, 460 parameters, goodness-of-fit on $F^2 = 1.135$, $R_1 = 0.065$, $wR_2 = 0.152$ [$I > 2\sigma(I)$], $R_1 = 0.084$, $wR_2 = 0.155$ (all data). Largest difference peak and hole: 2.45/-0.95 e Å⁻³ (near Ir).

4. Crystal structure determinations

Crystals of compounds **7**[Me₃SnCl₂] and **9**[Me₃SnCl₂] · Et₂O suitable for X-ray study were investigated with a Stoe Imaging Plate Diffraction System using graphite-monochromatized Mo K α radiation ($\lambda = 0.71073$ Å). Unit cell parameters were determined by least-squares refinements on the positions of 8000 reflections in the range $6.55^\circ < \theta < 22.25^\circ$ and $5.5^\circ < \theta < 21.8^\circ$, respectively. For **7**[Me₃SnCl₂] space group *Pbca* was uniquely determined. In the case **9**[Me₃SnCl₂] · Et₂O the anorthic lattice was consistent with space groups types *P1* and *P1* $\bar{1}$, but the latter proved to be the correct one in the course of structure refinements. Lp corrections were applied to all the intensity data. Due to the irregular shapes of the crystals semiempirical absorption corrections had to be applied in both cases ($T_{\min.} = 0.37$, $T_{\max.} = 0.87$ and $T_{\min.} = 0.31$, $T_{\max.} = 0.79$, respectively). The structures were solved by direct methods [18] and the positions of all but the hydrogen atoms of the methyl groups of the dichlorotrimethylstannate ions and the diethyl ether solvent molecule were found *via* ΔF -syntheses. Refinements by full-matrix least-squares calculations [19] on F^2 converged to the indicators above. Anisotropic displacement parameters were refined for all atoms heavier than hydrogen with the exception of C and O atoms of the diethyl ether. Idealized bond lengths and angles were used for the CH₃, CH₂ and CH groups; the riding model was applied for their H atoms. In addition, the H atoms of the CH₃ groups were allowed to rotate around the neighbouring C–C bonds. Isotropic displacement parameters of the H atoms were kept equal to 150%, 130% and 120% of the equivalent isotropic displacement parameters of the parent primary, secondary and “aromatic” carbon atoms, respectively. In the case of **9**[Me₃SnCl₂] · Et₂O the complete Et₂O molecule was treated as a rigid group with idealized bond lengths and angles assuming the all-*trans* conformation and a common isotropic displacement parameter for C and O atoms.

Supplementary material

CCDC 684387 and 684388 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References

- [1] F. Mathey, A. Mitschler, R. Weiss, *J. Am. Chem. Soc.* 99 (1977) 3537–3538.
- [2] For comprehensive reviews see: (a) P. Le Floch, *Coord. Chem. Rev.* 250 (2006) 627–681; (b) D. Carmichael, F. Mathey, *Top. Curr. Chem.* 220 (2002) 27–51; (c) F. Mathey, *Coord. Chem. Rev.* 137 (1994) 1–52.
- [3] C. Ganter, in: A. Börner (Ed.), *Phosphorus Ligands in Asymmetric Catalysis*, Wiley-VCH, 2008, pp. 393–407; G.C. Fu, *Acc. Chem. Res.* 39 (2006) 853–860; C. Ganter, *J. Chem. Soc., Dalton Trans.* (2001) 3541–3548; D. Carmichael, G. Goldet, J. Klankermayer, L. Ricard, N. Seeboth, M. Stankevič, *Chem. Eur. J.* 13 (2007) 5492–5502.
- [4] D. Carmichael, L. Ricard, F. Mathey, *Chem. Commun.* (1994) 1167–1168.
- [5] Y. Cabon, D. Charmichael, K. Forissier, F. Mathey, L. Ricard, N. Seeboth, *Organometallics* 26 (2007) 5468–5472.
- [6] C. Burney, D. Carmichael, K. Forissier, J.C. Green, F. Mathey, L. Ricard, *Chem. Eur. J.* 11 (2005) 5381–5390.
- [7] K. Forissier, L. Ricard, D. Carmichael, F. Mathey, *Chem. Commun.* (1999) 1273–1274.
- [8] K. Forissier, L. Ricard, D. Carmichael, F. Mathey, *Organometallics* 19 (2000) 954–956.
- [9] C. Burney, D. Carmichael, K. Forissier, J.C. Green, F. Mathey, L. Ricard, *Chem. Eur. J.* 9 (2003) 2567–2573.
- [10] G.E. Herberich, B. Ganter, *Inorg. Chem. Commun.* 4 (2001) 100–103.
- [11] F. Nief, L. Ricard, *Organometallics* 20 (2001) 3884–3890.
- [12] D. Carmichael, F. Mathey, L. Ricard, N. Seeboth, *Chem. Commun.* (2002) 2976–2977.
- [13] T. Arliguie, M. Ephritikhine, M. Lance, M. Nierlich, *J. Organomet. Chem.* 524 (1996) 293–297.
- [14] H. Werner, B. Klingert, A.L. Rheingold, *Organometallics* 7 (1988) 911–917.
- [15] (a) R. Loschen, C. Loschen, W. Frank, C. Ganter, *Eur. J. Inorg. Chem.* (2007) 553–561; (b) M. Westerhausen, M.H. Digeser, C. Gückel, H. Nöth, J. Knizek, W. Ponikwar, *Organometallics* 18 (1999) 2491–2496; (c) A.J. Ashe III, J.W. Kampf, S.M. Al-Taweel, *Organometallics* 11 (1992) 1491–1496; (d) A.J. Ashe III, J.W. Kampf, S.M. Al-Taweel, *J. Am. Chem. Soc.* 114 (1992) 372–374; (e) X. Sava, N. Mézailles, N. Maigrot, F. Nief, L. Ricard, F. Mathey, P. Le Floch, *Organometallics* 18 (1999) 4205; (f) M. Visseaux, F. Nief, L. Ricard, *J. Organomet. Chem.* 647 (2002) 139–144.
- [16] (a) F. Nief, F. Mathey, *Chem. Commun.* (1988) 770–771; (b) F. Nief, L. Ricard, F. Mathey, *Organometallics* 8 (1989) 1473–1477; (c) D. Carmichael, L. Ricard, F. Mathey, *Chem. Commun.* (1994) 2459–2460.
- [17] A. Breque, F. Mathey, P. Savignac, *Synthesis* (1981) 983–985.
- [18] G.M. Sheldrick, *SHELXS86*, Program for the Solution of Crystal Structures, University of Göttingen, Germany, 1985.
- [19] G.M. Sheldrick, *SHELXL97*, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.