Inorganic Chemistry

Communication

pubs.acs.org/IC

Reactivity of a Mononuclear Iridium(I) Species Bearing a Terminal Phosphido Fragment Embedded in a Triphosphorus Ligand

Yann Gloaguen,[†] Wesley Jacobs,[†] Bas de Bruin,[†] Martin Lutz,[‡] and Jarl Ivar van der Vlugt*[,†]

[†]Homogeneous & Supramolecular Catalysis, van 't Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 904, 1098 XH Amsterdam, The Netherlands

[‡]Department of Crystal and Structural Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands

Supporting Information

ABSTRACT: The first example of an iridium(I) species bearing a terminal phosphido (PR_2^-) ligand is reported. This stable compound shows well-behaved reactivity toward various electrophiles, owing to its exposed phosphorus lone pair, allowing reversible protonation, selective alkylation, isolation of a phosphidoborane of iridium, and generation of a phosphido-bridged iridium(I)−gold(I) dinuclear species.

The coordination chemistry of monoanionic phosphido ligands (PR_2^-) to main-group elements or transition metals is well developed, with preference for the ligand to act as a bridging moiety spanning two metal centers.[1] In the case of terminal phosphido coordination, there are two extreme bonding situations of this monoanionic scaffold to a metal center, i.e., only σ-bond coordination and a single metal−phosphorus bond (2e donor) or σ−π coordination (4e donor) via additional π-bond interaction between the phosphorus lone pair and a suitable metal d orbital, yielding formal double-bond character (Figure 1). The latter results in trigonal-planar geometry around phosphorus, whereas the former implies a trigonal-pyramidal phosphorus atom with its lone pair pointing away from the metal center, imparting residual Lewis basicity at this phosphorus donor. As a result, this type of phosphide can be regarded as coordinatively unsaturated, despite its σ-bonding interaction with the metal center. Such metal phosphido complexes may therefore act as (metallo)ligands (Figure 1).

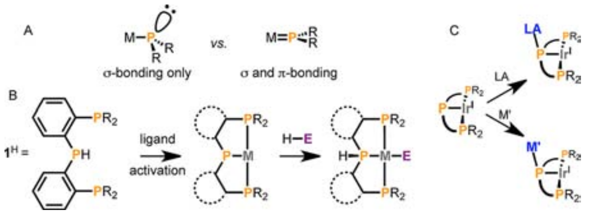


Figure 1. (A) Trigonal pyramidal vs trigonal planar terminal phosphide coordination, (B) concept of a cooperative P^H/P^- couple based on $\mathbf{1^H}$, and (C) metalloligand reactivity of a terminal $Ir^I(PR_2)$ species.

Phosphidoboranes (also termed phosphanyl borohydrides) are key intermediates during the synthesis of chiral phosphine ligands and the formation of inorganic P−B polymers via catalytic dehydrocoupling of phosphineboranes and C−P bond formation.[2] Despite their importance, structurally well-characterized examples of complexes incorporating a phosphidoborane adduct are mainly limited to alkali and some group 8 (iron and ruthenium) and group 10 (palladium and platinum) metals.[3,4] Most iridium phosphido complexes exist as di- or multinuclear species, and low-valent iridium complexes featuring a terminal phosphido are elusive.[5] As a result, little is known about the stability of these species or the residual reactivity of the phosphide fragment. For example, no phosphidoborane adduct of iridium has been reported to date. Heterodinuclear analogues bearing a bridging iridium(I) phosphido unit are also unknown.

Currently, there is ongoing interest in the application of (monoanionic) "pincer" ligands to tune the properties of late transition metals, especially in combination with reactive ligand design and metal−ligand bifunctional bond activation processes.[6] To the best of our knowledge, bona fide phosphido-based systems have not yet been considered (Figure 1).[7]

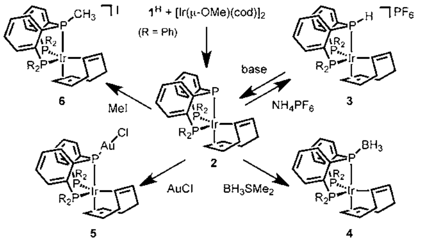
Given our interest in reactive ligands and their potential applications,[8] we envisaged bis[(2-diphenylphosphino)phenyl]-phosphine ($\mathbf{1^H}$) as a monoanionic scaffold for group 9 metals. Copper(I) dimers with $\mathbf{1}^-$ as the dinucleating entity were previously reported,[9] and coordination of $\mathbf{1}^-$ to palladium(II) or platinum(II) afforded square-planar mononuclear complexes.[10] In contrast herewith, we reported combined experimental and computational data on the group 9 metal rhodium(I), wherein this ligand coordinated preferentially as the intact PP^HP fragment, withstanding deprotonation.[11] We herein describe the coordination of monoanionic $\mathbf{1}^-$ onto iridium(I) and its selective reactivity with various electrophiles to yield stable, well-defined species.

In pursuit of an iridium(I) species bearing $\mathbf{1}^-$ rather than $\mathbf{1^H}$, which would also lead to the first known terminal iridium(I) phosphido species, we initially turned to $[Ir(\mu\text{-}Cl)(coe)_2\}_2]$ and related dimeric iridium precursors, but these reactions led to multiple products, as indicated by ^{31}P and ^{1}H NMR spectroscopy, and attempts to isolate a single species failed. This is reminiscent of our results with rhodium[11] as well as reported reactions with related PN^HP ligands.[12] However, in contrast to other synthetic protocols for such bis(phosphinoaryl)amine systems,[13] deprotonation of ligand $\mathbf{1^H}$ or formation of a lithiated derivative prior to introduction of a suitable (halide-based) metal precursor did not proceed cleanly. Efforts to enforce coordination of ligand $\mathbf{1}^-$ using, e.g., $[\{Ir(\mu\text{-}OH)(coe)_2\}_2]$ or

Received: October 23, 2012
Published: January 29, 2013

[{Ir(μ-OMe)(coe)$_2$}$_2$] failed to give selective reactions. Gratifyingly, the reaction of [{Ir(μ-OMe)(cod)}$_2$][14] with 2 mol equiv of $\mathbf{1}^{\mathbf{H}}$ generated a single isolable product in 81% yield (Scheme 1).

Scheme 1. Synthesis and Versatile Reactivity of Complex 2



An IR spectroscopic comparison of this moderately air-stable beige solid with free ligand $\mathbf{1}^{\mathbf{H}}$ indicated deprotonation of the secondary phosphine upon coordination. The corresponding ^{31}P NMR spectrum showed signals at δ 28.8 (phosphine) and 66.7 (phosphide). No P−P coupling was observed, suggestive of a reduced σ character of the iridium−phosphide bond. Two signals for nonequivalent HC═CH groups of a coordinated cod fragment were observed in the ^{1}H NMR spectrum, indicating different coordination environments. This was confirmed by the observation of two characteristic signals in the ^{13}C NMR spectrum (at δ 78.8 and 54.7), leading us to formulate this complex as Ir(*fac*-**1**)(cod) (**2**), featuring a terminal iridium phosphido unit embedded within the facially coordinated monoanionic donor ligand $\mathbf{1}^-$.

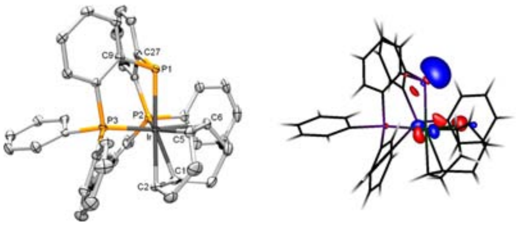


Figure 2. Left: ORTEP plot of complex **2**. Solvent and hydrogen atoms are omitted for clarity. Right: calculated highest occupied molecular orbital (HOMO) for **2**.

Recrystallization of complex **2** from toluene led to single crystals suitable for X-ray diffraction (Figure 2 and S24 for details). The difference Fourier map did not indicate protonation at P$_1$. The neutral complex features the monoanionic PP$^-$P scaffold $\mathbf{1}^-$, with the phosphido unit occupying an axial position in the distorted trigonal-bipyramidal geometry around iridium(I). As a result, $\mathbf{1}^-$ acts as a facial tridentate ligand rather than the meridional "pincer"-like orientation observed with palladium.[10,11] The acute ∠P$_1$−Ir−P$_2$ [84.781(15)°] and ∠P$_2$−Ir−P$_3$ [107.964(14)°] indicate a high degree of ligand backbone rigidity, and there is no apparent mirror plane through Ir−P$_1$. The Ir−P bond lengths are similar, prohibiting a formal distinction in donor character between the phosphido (P$_1$) and phosphine (P$_2$ and P$_3$) donors. For d^8 metal complexes with a trigonal-bipyramidal geometry, the strongest σ-donor ligands generally bind in the axial positions, while π-back-bonding is typically more pronounced in the equatorial plane.[15] Interestingly, Calimano and Tilley reported the structure of Ir(*fac*-PNP)(cod) (**A**), generated via deprotonation of the cationic analogue [Ir(*mer*-PN$^{\mathrm{H}}$P)(cod)]Cl.[16] In contrast to our findings, the molecular structure for **A** featured a trigonal-planar nitrogen atom and, hence, a very different orientation of the backbone phenyl rings compared to **2**.

Given the observed geometric features of **2**, we were interested in probing reversible protonation at the phosphido bridgehead. The addition of 1 equiv of NH_4PF_6 to a solution of **2** in CH_2Cl_2 led to a darkening of the reaction mixture, concomitant with the facile formation of cationic [Ir(*fac*-$\mathbf{1}^{\mathbf{H}}$)(cod)]PF$_6$ (**3**). The P−H fragment is readily observed in the ^{1}H NMR spectrum [δ 6.31 (dt, $^1J_{\mathrm{P-H}}$ = 408 Hz, $^4J_{\mathrm{P-H}}$ = 4.4 Hz)], with further evidence from the ^{31}P NMR spectrum [δ 45.9 (dt, $^1J_{\mathrm{P-H}}$ = 408 Hz, $J_{\mathrm{P-P}}$ = 14.3 Hz), 25.5 (d, $J_{\mathrm{P-P}}$ = 14.3 Hz)] as well as IR spectroscopy ($\nu_{\mathrm{P-H}}$ 2330 cm^{-1}). The secondary phosphine in species **3** is smoothly deprotonated by KO^{t}Bu,[17] which is in stark contrast to our earlier findings on Rh(PP$^{\mathrm{H}}$P) complexes.[10,18]

Density functional theory (DFT) analysis of various five-coordinated Ir(**1**)(ethene)$_2$ model structures (see the Supporting Information, SI) confirmed the observed rare *fac* coordination for $\mathbf{1}^-$ to be preferred over the hypothetical *mer* analogues for iridium(I). The calculated bond order (1.003) for the Ir−P bond in **2** is indicative of almost exclusive σ-bonding character with little involvement of the exposed phosphorus lone pair, in agreement with the calculated highest molecular orbital (HOMO) of **2** (Figure 1). Thus, complex **2** contains a formal terminal phosphido pivot that likely exhibits significant (metallo)phosphine character.

To support this hypothesis, we investigated reactions with several electrophiles. The addition of an equimolar amount of BH_3SMe_2 to a solution of **2** in dichloromethane resulted in a beige solid after workup. The ^{31}P NMR spectrum revealed two signals at δ 53.0 (br s, 1P) and 29.3 (d, $J_{\mathrm{P-P}}$ = 13 Hz, 2P). A chemical shift difference $\Delta\delta$ of −13.6 ppm was noted for the pivotal phosphorus atom relative to **2**. A signal at δ −33.5 for the BH_3 group was observed in the corresponding ^{11}B{^{1}H} NMR spectrum. Fast atom bombardment mass spectrometry (MS) data (868.23 [M$^+$]) were consistent with the formation of iridium(I) phosphidoborane species Ir(*fac*-**1**·BH$_3$)(cod) (**4**; see Figure S25 for the DFT-calculated HOMO). This borane adduct did not react with DABCO at room temperature. Nucleophilic metalloligand **2** also reacted smoothly with 1 equiv of AuCl, resulting in the formation of a beige species with NMR spectroscopic features similar to those of parent **2** [δ 69.7 (t, $J_{\mathrm{P-P}}$ = 14 Hz, 1P), 27.8 (d, $J_{\mathrm{P-P}}$ = 14 Hz, 2P)], for which MS data indicated the formation of complex Ir(*fac*-**1**·AuCl)(cod) (**5**). The molecular structures of **4** and **5** are depicted in Figure 3 (see Figure S26 for details).

Both complexes show significant deviation from ideal C_2 symmetry at the P$_1$ pivot. For **4**, this becomes apparent from, e.g., the torsion angles B$_1$−P$_1$−Ir−C$_5$ [0.08(9)°] and B$_1$−P$_1$−Ir−C$_6$ [−38.26(9)°]. The BH$_3$ group is moved out-of-plane, with the torsion angle B$_1$−P$_1$−Ir$_1$−C$_{5-6}$ being −19.15(8)° as a result

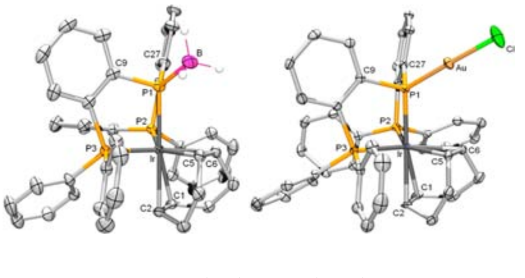


Figure 3. ORTEP plots of **4** (left) and **5** (right). Solvent and hydrogen atoms are omitted for clarity, except for BH$_3$.

of the rigid PPP backbone, with an acute $\angle C_9-P_1-C_{27}$ of approximately 101°. Overall, the Ir(**1**) framework changes only marginally upon coordination of the BH_3 or AuCl fragment.[19] Alkylation with MeI also occurs selectively at the P bridgehead to yield species **6**, bearing a triphosphine ligand (see the SI). Selective oxidation of the phosphide unit was achieved using excess Me_3NO to give phosphido oxide **7**, which was recrystallized from C_6H_6 (see Figure S27). Selective removal of the cod ligand in **2** using H_2 (50 bar), syngas (55 bar), silane, or $ZrCl_4$ was not successful. Also, protonated species **3** resisted hydrogenation of cod with 50 bar of H_2 for 5 days. The presence of the strongly coordinated cod ligand within the five-coordinated geometry of **2** has so far hampered bifunctional H−E bond activation.

In conclusion, we have obtained the first mononuclear group 9 complex, containing **1** as the facial ligand, which bears a previously unknown terminal phosphidoiridium(I) motif. The P bridgehead in complex **2** shows well-behaved reactivity, i.e., facile protonation and alkylation as well as Lewis basic coordination to BH_3 and AuCl. We are currently studying bimetallic compounds based on metalloligand **2** for application in catalysis.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental, DFT, and crystallographic data, CIF files, graphics, and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: j.i.vandervlugt@uva.nl.

Author Contributions

The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was financially supported by NWO-ACTS (ASPECT 053.62.029) and ERC Starting Grant EuReCat, Grant Agreement 279097. The COST network CM0802 "PhoSciNet", Prof. J. N. H. Reek, and Dr. A. W. Ehlers are thanked for suggestions.

■ REFERENCES

(1) Mastrorilli, P. *Eur. J. Inorg. Chem.* **2008**, 4835−4850.

(2) (a) Blank, N. F.; Moncarz, J. R.; Brunker, T. J.; Scriban, C.; Anderson, B. J.; Amir, O.; Glueck, D. S.; Zakharov, L. N.; Golen, J. A.; Incarvito, C. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **2007**, *129*, 6847−6858. (b) Lee, K.; Clark, T. J.; Lough, A. J.; Manners, I. *Dalton Trans.* **2008**, 2732−2740. (c) Waterman, R. *Curr. Org. Chem.* **2008**, *12*, 1322−1339. (d) Chan, V. S.; Chiu, M.; Bergman, R. G.; Toste, F. D. *J. Am. Chem. Soc.* **2009**, *131*, 6021−6032.

(3) (a) Pican, S.; Gaumont, A.-C. *Chem. Commun.* **2005**, 2393−2395. (b) Jaska, C. A.; Lough, A. J.; Manners, I. *Dalton Trans.* **2005**, 326−331. (c) Kückmann, T. I.; Dornhaus, F.; Bolte, M.; Lerner, H.-W.; Holthausen, M. C.; Wagner, M. *Eur. J. Inorg. Chem.* **2007**, 1989−2003. (d) Izod, K.; Watson, J. M.; Clegg, W.; Harrington, R. W. *Eur. J. Inorg. Chem.* **2012**, 1696−1701.

(4) Recently, the first example of copper phosphidoborane was reported: Abdellah, I.; Bernoud, E.; Lohier, J.-F.; Alayrac, C.; Toupet, L.; Lepetit, C.; Gaumont, A.-C. *Chem. Commun.* **2012**, *48*, 4088−4090.

(5) Monomeric iridium(III) examples are known: (a) Ebsworth, E. A. V.; Gould, R. O.; MacManus, N. T.; Pilkington, N.; Rankin, D. W. H. *J. Chem. Soc., Dalton Trans.* **1984**, 2561−2567. (b) Fryzuk, M. D.; Bhangu, K. *J. Am. Chem. Soc.* **1988**, *103*, 961−963. (c) Fryzuk, M. D.; Joshi, K.; Chadha, R. K.; Rettig, S. J. *J. Am. Chem. Soc.* **1991**, *113*, 8724−8736.

(6) (a) van der Vlugt, J. I.; Reek, J. N. H. *Angew. Chem., Int. Ed.* **2009**, *48*, 8832−8846. (b) Zweifel, T.; Naubron, J.-V.; Grützmacher, H. *Angew. Chem., Int. Ed.* **2009**, *48*, 559−563. (c) Zhu, Y.; Chen, C.-H.; Fafard, C. M.; Foxman, B. M.; Ozerov, O. V. *Inorg. Chem.* **2011**, *50*, 7980−7987. (d) MacInnis, M. C.; McDonald, R.; Ferguson, M. J.; Tobisch, S.; Turculet, L. *J. Am. Chem. Soc.* **2011**, *133*, 13622−13633. (e) Gunanathan, C.; Milstein, D. *Acc. Chem. Res.* **2011**, *44*, 588−602. (f) van der Vlugt, J. I. *Eur. J. Inorg. Chem.* **2012**, 363−375. (g) Schneider, S.; Meiners, J.; Askevold, B. *Eur. J. Inorg. Chem.* **2012**, 412−429. (h) Harman, W. H.; Peters, J. C. *J. Am. Chem. Soc.* **2012**, *134*, 5080−5082. (i) Zech, A.; Haddow, M. F.; Othman, H.; Owen, G. R. *Organometallics* **2012**, *32*, 6753−6760. (j) Yoshinari, A.; Tazawa, A.; Kuwata, S.; Ikariya, T. *Chem.—Asian J.* **2012**, *7*, 1417−1425.

(7) Cooperative E−H bond activation by a Pt(NHP) complex with phosphido/phosphenium character: Pan, B.; Bezpalko, M. W.; Foxman, B. M.; Thomas, C. M. *Dalton Trans.* **2012**, *41*, 9083−9090.

(8) (a) van der Vlugt, J. I.; Pidko, E. A.; Vogt, D.; Lutz, M.; Spek, A. L. *Inorg. Chem.* **2009**, *48*, 7513−7515. (b) van der Vlugt, J. I.; Siegler, M. A.; Janssen, M.; Vogt, D.; Spek, A. L. *Organometallics* **2009**, *29*, 7025−7032. (c) van der Vlugt, J. I.; Lutz, M.; Pidko, E. A.; Vogt, D; Spek, A. L. *Dalton Trans.* **2009**, 1016−1023. (d) van der Vlugt, J. I. *Angew. Chem., Int. Ed.* **2010**, *49*, 252−255. (e) van der Vlugt, J. I.; Pidko, E. A.; Bauer, R. C.; Gloaguen, Y.; Rong, M. K.; Lutz, M. *Chem.—Eur. J.* **2011**, *17*, 3850−3854. (f) Lindner, R.; van den Bosch, B.; Lutz, M.; Reek, J. N. H.; van der Vlugt, J. I. *Organometallics* **2011**, *30*, 499−510. (g) de Boer, S. Y.; Gloaguen, Y.; Lutz, M.; van der Vlugt, J. I. *Inorg. Chim. Acta* **2012**, *380*, 336−342. (h) de Boer, S. Y.; Gloaguen, Y.; Reek, J. N. H.; Lutz, M.; van der Vlugt, J. I. *Dalton Trans.* **2012**, *41*, 11276−11283.

(9) Mankad, N. P.; Rivard, E.; Harkins, S. B.; Peters, J. C. *J. Am. Chem. Soc.* **2005**, *127*, 16032−16033.

(10) (a) Mazzeo, M.; Lamberti, M.; Massa, A.; Scettri, A.; Pellecchia, C.; Peters, J. C. *Organometallics* **2008**, *27*, 5741−5743. (b) Mazzeo, M.; Strianese, M.; Kühl, O.; Peters, J. C. *Dalton Trans.* **2011**, *40*, 9026−9033. For a related NPN ligand, see: (c) MacInnis, M. C.; McDonald, R.; Turculet, L. *Organometallics* **2011**, *30*, 6408−6415.

(11) Bauer, R. C.; Gloaguen, Y.; Lutz, M.; Reek, J. N. H.; de Bruin, B.; van der Vlugt, J. I. *Dalton Trans.* **2011**, *40*, 8822−8829.

(12) Friedrich, A.; Ghosh, R.; Kolb, R.; Herdtweck, E.; Schneider, S. *Organometallics* **2009**, *28*, 708−718.

(13) Weng, W.; Yang, L.; Foxman, B. M.; Ozerov, O. V. *Organometallics* **2004**, *23*, 4700−4703.

(14) Uson, R.; Oro, L. A.; Cabeza, J. A.; Bryndza, H. E.; Stepro, M. P. *Inorg. Synth.* **1985**, *23*, 126−130.

(15) Rossi, A. R.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 365−374.

(16) Calimano, E.; Tilley, T. D. *Dalton Trans.* **2010**, *39*, 9250−9263.

(17) Reversible protonation of a coordinated PR_2^- ligand: (a) Bohle, D. S.; Jones, T. C.; Rickard, C. E. F.; Roper, W. R. *J. Chem. Soc., Chem. Commun.* **1984**, 865−867. (b) Scriban, C.; Glueck, D. S.; DiPasquale, A. G.; Rheingold, A. L. *Organometallics* **2006**, *25*, 5435−5448.

(18) Deprotonation was not demonstrated for the related *fac*-PNP structure **A**.[15] *mer*-PNP ligands can undergo shuttling between amine and amido stages: (a) Friedrich, A.; Drees, M.; Käß, M.; Herdtweck, E.; Schneider, S. *Inorg. Chem.* **2010**, *49*, 5482−5494. (b) Gregor, L. C.; Chen, C.-H.; Fafard, C. M.; Fan, L.; Guo, C.; Foxman, B. M.; Gusev, D. G.; Ozerov, O. V. *Dalton Trans.* **2010**, *39*, 3195−3202.

(19) Rigid PP_3: (a) Wassenaar, J.; de Bruin, B.; Siegler, M. A.; Spek, A. L.; Reek, J. N. H.; van der Vlugt, J. I. *Chem. Commun.* **2010**, *46*, 1232−1234. (b) Wassenaar, J.; Siegler, M. A.; Spek, A. L.; de Bruin, B.; Reek, J. N. H.; van der Vlugt, J. I. *Inorg. Chem.* **2010**, *49*, 6495−6508.

■ NOTE ADDED AFTER ASAP PUBLICATION

Due to a production error, this paper was published on the Web on January 29, 2013, with errors in the SI file. The corrected version was reposted on February 1, 2013.