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Phosphinidenes

Nucleophilic Phosphinidene Complexes: Access and Applicability

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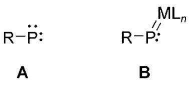
carbene homologues · phosphinidene ligands · phosphorus · synthesis design · transition metals

Syntheses, properties, and reactivities of nucleophilic phosphinidene complexes $[L_nM{=}P{-}R]$ are reviewed. Emphasis is placed on the electronic tuning of this emerging class of phosphorus reagents, using different ancillary ligands and coordinatively unsaturated transition-metal moieties. The difference in applicability of the established stable 18-electron and transient 16-electron phosphinidenes is addressed.

1. Introduction



Scheme 1. Free (**A**) and η^1-complexed phosphinidene (**B**).

Phosphinidenes[1] (phosphanylidenes,[2] R−P, **A**; Scheme 1) are the phosphorus analogues of carbenes (R_2C)[3] and nitrenes (R−N).[4] These exceedingly reactive phosphorus species have been detected only in the gas phase (by mass spectrometry) and in glassy and cryogenic matrices (by EPR, IR, and UV spectroscopy).[5] Their chemistry remains to be fully explored,[6] which distinguishes them from the carbenes, which have seen explosive growth. However, terminal transition-metal-complexed phosphinidenes ($[L_nM{=}P{-}R]$, **B**; Scheme 1), which are the phosphorus analogues of the well-established carbene complexes, appear to be valuable synthons with rapidly expanding chemistries.[7–10] These advances were enabled by the discovery in the 1980s of the transient electrophilic species $[(OC)_5W{=}P{-}Ph]$ by the group of Mathey[11] and of the isolable nucleophilic phosphinidene complex $[Cp_2W{=}P{-}Mes^*]$ by Lappert and co-workers ($Cp = C_5H_5$, $Mes^* = 2,4,6\text{-}t\mathrm{Bu}C_6H_2$).[12] Illustrative of the ensuing rapid progress in this field are two reviews by Cowley, one published in 1988, entitled “The Quest for Terminal Phosphinidene Complexes”[13a] and the other in 1997 “Terminal Phosphinidene and Heavier Congeneric Complexes. The Quest is Over”.[13b] Much has happened since, as is emphasized in this Minireview, which focuses on neutral nucleophilic η^1-phosphinidene complexes. To date, these compounds have been considered to have limited applicability, sharply contrasting their electrophilic counterparts,[1,8] but their potential is far greater than believed.

2. Transition-Metal Ligation

To start, it is important to recognize the impact of a transition-metal group on the phosphinidene R−P. Terminally complexed phosphinidenes are either nucleophilic (Schrock type)[14] or electrophilic (Fischer type)[15] at the phosphorus atom. An extensive density functional study[16] on $[L_nM{=}PH]$ (M = Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Fe, Ru, Os, Co, Rh, Ir and L = CO, PH_3, Cp) revealed that the philicity and chemical reactivity of the phosphinidene complex is influenced mainly by the metal’s spectator ligand L. Those ligands with strong σ-donor capabilities increase the electron density on the phosphorus atom, enhancing its nucleophilicity. Conversely, spectator ligands with strong π-acceptor capabilities lower the charge concentration on P, causing electrophilic behavior. Illustrative is the difference between electrophilic $[(OC)_4Fe{=}PH]$ and nucleophilic $[Cp_2Cr{=}PH]$, which is a reflection of the different magnitude in which charge is transferred from the frontier orbitals of the transition-metal fragments to the phosphorus atom. Indeed, all reported phosphinidene complexes with only CO ligands, such as $[(OC)_nM{=}P{-}R]$ (M = W, Mo, Cr, $n = 5$; M = Fe, $n = 4$), are known to be transient electrophiles, generated in situ from appropriate precursors. Their insertion into σ bonds, addition to π bonds, and coordination to lone pairs is well-documented and reviewed.[1,8] More diversity in ancillary ligands is available in cationic complexes $[L_nM{=}P{-}R]^+$, of which stable ones[17] with limited reactivity have been reported.[17e,f,18] The diversity in ligands and transition metals is by far the largest for the nucleophilic phosphinidene complexes, the topic of this Minireview. Before advancing, it must be noted that the M=P bonds of all $[L_nM{=}P{-}R]$ complexes have genuine

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double-bond character, as established by a DFT bond energy analysis, from which quantitative σ- and π-bond strengths could be determined.[16] The M=P interaction increases on going from the first- to the second- and third-row transition metals. Earlier reviews focused mainly on the structural properties, including the M=P−R angle, of the nucleophilic phosphinidenes. This Minireview emphasizes first the different methodologies to access these entities and then addresses their chemical applicability.

Halil Aktaş was born in 1976 in the Karşıyaka district of the province İzmir in Turkey. He obtained his M.Sc. in Organic Chemistry at the VU University Amsterdam in 2003 and his Ph.D. on nucleophilic phosphinidenes at the same institute under the guidance of Koop Lammertsma in 2009. He is currently working at Tate and Lyle on renewable ingredients.

Chris Slootweg was born in Haarlem, The Netherlands, in 1978 and studied at the VU University Amsterdam. During his M.Sc. at the University of Sussex (M. F. Lappert) he was exposed to silicon chemistry and at the University of Amsterdam (P. W. N. M. van Leeuwen) to homogeneous catalysis. He received his Ph.D. in 2005. As a postdoctoral fellow he studied C−H activation in the group of P. Chen at the ETH Zürich. In 2006, he returned as an assistant professor to the VU University Amsterdam, where he is exploring his interests in main-group and organometallic chemistry.

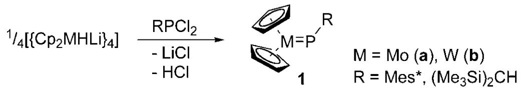
Koop Lammertsma was born in Makkum, The Netherlands, and was educated at the Universities of Groningen (M.Sc. 1974) and Amsterdam (Ph.D. 1979). Postdoctoral work with F. Sondheimer (London), P. von R. Schleyer (Erlangen-Nürnberg), and Nobel laureate G. A. Olah (USC) exposed him to physical-organic and computational chemistry. In 1983 he moved to the University of Alabama at Birmingham, USA, becoming Full Professor in 1992. In the same year he served as program officer in the chemistry program of the NSF. In 1996 he moved to the VU University Amsterdam, The Netherlands, where he integrated his synthetic and theoretical research on low-valent organophosphorus chemistry.

3. Generating Nucleophilic Phosphinidene Complexes

3.1. Salt Metathesis and Elimination

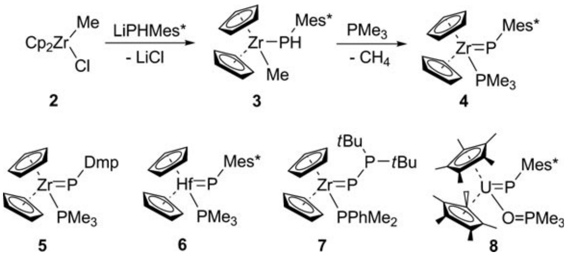
The most common route toward nucleophilic phosphinidene complexes is the combination of a metal complex with a halogenated species under expulsion of M^+X^-. There are two possibilities, treating a Li^+ metallocene hydride with a chlorophosphine and conversely treating a transition-metal halide complex with a lithium phosphide, but variations on this salt metathesis theme exist.

The first stable 18-electron phosphinidene complexes were synthesized by Lappert and co-workers,[12] who treated lithium metallocene hydride $[\{Cp_2MHLi\}_4]$ with dichlorophosphine $RPCl_2$ (R = Mes*, $(Me_3Si)_2CH$) to obtain $[Cp_2M{=}PR]$ (**1a**,**b**, M = Mo, W, respectively) as stable, red crystalline materials (Scheme 2).[12] The low-field ^{31}P NMR spectroscopy chemical shifts (R = Mes*; Mo (**1a**) $\delta = 799.5$ ppm, W (**1b**) $\delta = 661.1$ ppm) proved to be characteristic for terminal phosphinidene complexes.[12] The X-ray crystal structures show a M=P double bond of 2.370(2) Å for the molybdenum complex[12] and of 2.349(5) Å for the tungsten complex,[12] with bent M-P-Mes* angles of 115.8(2)° and 114.8(5)°, respectively.



Scheme 2. Salt metathesis with dichlorophosphines.

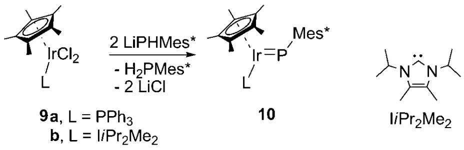
Stephan and co-workers synthesized the first early-transition-metal complex, zirconium phosphinidene $[Cp_2(Me_3P)Zr{=}P{-}Mes^*]$ (**4**) by salt metathesis of zirconocene dichloride and lithium supermesitylphosphide[19] and from zirconium phosphide $[Cp_2(Cl)ZrP(H)Mes^*]$ using an alkali-metal base,[20] both in the presence of PMe_3.[19,20] The X-ray crystal structure reveals a short Zr=P bond of 2.505(4) Å, a Zr-P-Mes* angle of 101.4(1)°, and a long $Zr{-}PMe_3$ bond of 2.741(5) Å, thus indicating weak bonding of the ancillary ligand. The chemical shift of the phosphinidene in the ^{31}P NMR spectrum is detected at $\delta = 792.7$ ppm. A superior route with a near quantitative yield is the reaction of chlorobis(η^5-cyclopentadienyl)methylzirconium (**2**) with lithium supermesitylphosphide and subsequent loss of methane from the incipient **3** in the presence of PMe_3 (Scheme 3).[19b] Using a similar procedure, Protasiewicz and co-workers reported the related phosphinidene complex $[Cp_2(Me_3P)Zr{=}P{-}Dmp]$ (**5**, Dmp = 2,6-$Mes_2C_6H_3$, Mes = 2,4,6-$Me_3C_6H_2$, Scheme 3).[21] Salt metathesis and Lewis base stabilization also enabled the synthesis of hafnium phosphinidene $[Cp_2(Me_3P)Hf{=}P{-}Mes^*]$ (**6**),[22] the terminally bonded phosphinophosphinidene complex $[Cp_2(PhMe_2P)Zr{=}P{-}PtBu_2]$ (**7**),[23] and the uranium



Scheme 3. Metal-complexed phosphinidenes synthesized using salt metathesis and Lewis base stabilization.

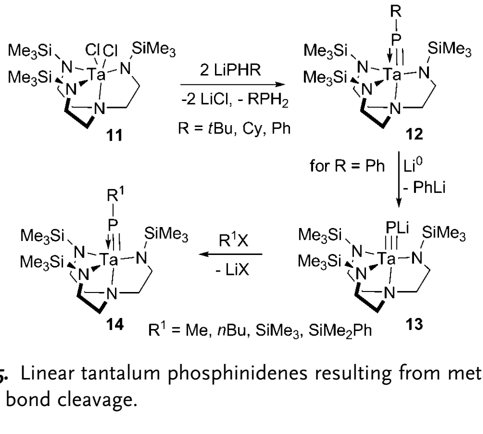
complex [Cp*$_2$(Me$_3$PO)U=P−Mes*] (**8**, Cp* = C$_5$Me$_5$, Scheme 3).[24] For all of these compounds, bent M=P−R bonding is indicated by ^{31}P NMR spectroscopic data (**6** δ = 671, **7** 728, **8** 71 ppm) and solid-state structures (M-P-C/P **7** 115.53(16), **8** 143.7(3) Å).

Salt metathesis was shown by Lammertsma and co-workers to be equally applicable to the late transition metal iridium, tolerating different ancillary ligands, such as PPh$_3$ and the N-heterocyclic carbene (NHC) I*i*Pr$_2$Me$_2$, together with a Cp* ligand.[25] Treating iridium dichloride complex **9** (**a** L = PPh$_3$, **b** L = I*i*Pr$_2$Me$_2$) with LiPHMes* provided **10a**,**b** (Scheme 4).[25] NHC-ligated iridium phosphinidene complex **10b**, characterized by an X-ray crystal structure, strongly resembles phosphane analogue **10a**; both show the expected bending (Ir-P-Mes* **10a** 113.73(7)°, **10b** 110.76(6)°) for a phosphinidene complex with typical M−P double bonding (Ir=P **10a** 2.2121(5), **10b** 2.1959(5) Å).[25] The difference in the resonances in their ^{31}P NMR spectra (**10a** δ = 686.6 ppm, **10b** δ = 560.0 ppm) is caused by the strong σ-donor and moderate π-acceptor capabilities of the NHC ligand rather than by geometrical differences.[25]



Scheme 4. Phosphane (**10a**) and N-heterocyclic carbene (**10b**) functionalized iridium phosphinidenes.

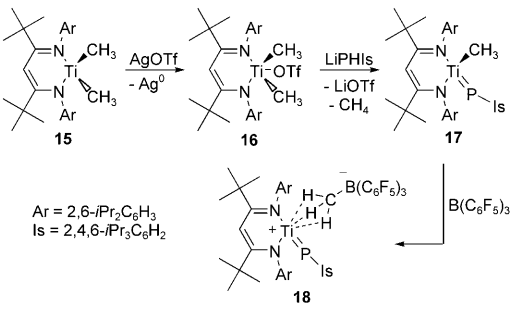
A series of tantalum phosphinidenes [[N$_3$N]Ta≡P−R] (**12**, [N$_3$N] = (Me$_3$SiNCH$_2$CH$_2$)$_3$N; R = *t*Bu, Cy, Ph; Cy = cyclohexyl) was reported by Schrock and co-workers, who condensed tantalum dichloride complex **11** with lithium phosphides (Scheme 5).[26] The large tetradentate triamidoamine ligand [N$_3$N] bearing trimethylsilyl groups ensures effective stabilization of the nucleophilic phosphinidene unit but narrows the space available to it. As a result, the Ta-P-R geometry is almost linear (Cy 170.9°), thus enforcing both Ta≡P pseudo-triple bonding (Cy 2.145(7) Å) and a high-field chemical shift for the phosphinidene in the ^{31}P NMR spectrum (δ = 175.1–227.3 ppm). The mechanism by which the phosphinidene complex is generated is not clear. The Ta≡P multiple bond may be formed by dehydrohalogenation with a second phosphide acting as base, whereas a proposed alternative path invokes α-proton abstraction from the tantalum bisphosphide.



Scheme 5. Linear tantalum phosphinidenes resulting from metathesis and P−C bond cleavage.

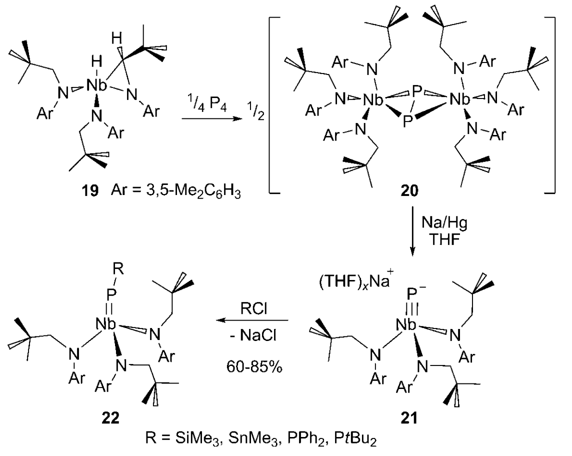
Interestingly, the phosphinidene substituent P−R of **12** is exchangeable. Reaction of the phenyl derivative with lithium afforded terminal phosphido complex [[N$_3$N]Ta≡P]$^-$ (**13**, Scheme 5),[27] which has a low-field resonance in the ^{31}P NMR spectrum at δ = 575 ppm, in concurrence with a phosphide complex. Subsequent reaction at −35 °C with organic halides afforded tantalum phosphinidene complexes [[N$_3$N]Ta=P−R^1] (**14**; R^1 = Me, *n*Bu, SiMe$_3$, SiMe$_2$Ph).

Mindiola's group used a sterically hindered β-diketiminate ligand in the reaction of a titanium complex with a lithium phosphide.[28] The process starts by one-electron oxidation of titanium dialkyl complex **15** with AgOTf, with subsequent reaction of **16** with LiPHIs (Is = 2,4,6-*i*Pr$_3$C$_6$H$_2$), presumably giving putative titanium phosphide [($^{t\mathrm{Bu}}$nacnac)Ti(Me)$_2$−PHIs] and, on loss of methane, phosphinidene complex [($^{t\mathrm{Bu}}$nacnac)(Me)Ti=P−Is] (**17**, $^{t\mathrm{Bu}}$nacnac = ArNC(*t*Bu)CHC(*t*Bu)NAr; Scheme 6). The diagnostic chemical shift at δ = 231.5 ppm in the ^{31}P NMR spectrum, the large Ti-P-Is angle of 159.95(7)°, and the short Ti=P bond of 2.1644(7) Å reveal a pseudo-linear titanium phosphinidene complex. Treatment with tris(pentafluorophenyl)borane caused methide abstraction to yield the terminal phosphinidene zwitterion [($^{t\mathrm{Bu}}$nacnac)Ti=P−Is{H$_3$CB(C$_6$F$_5$)$_3$}] (**18**), for which the X-ray crystal structure showed a short Ti=P bond (2.1512(4) Å), a linear Ti-P-Is unit (176.03(5)°), and an essentially departed methide group (Ti−CH$_3$ 2.405(3) Å).



Scheme 6. Titanium phosphinidene formed by salt metathesis with subsequent α-hydrogen abstraction and methide elimination.

Another protocol using a transition-metal-complexed phosphide was developed by Cummins and Figueroa. With niobaziridine hydride complex [Nb(H)(η^2-*t*Bu(H)C=NAr)-(NNpAr)$_2$] (**19**, Np = neopentyl, Ar = 3,5-Me$_2$C$_6$H$_3$),[29a] they activated white phosphorus (P$_4$) to form bridged diphosphide complex [(μ^2:η^2,η^2-P$_2$){Nb(NNpAr)$_3$}$_2$] (**20**), which on treatment with sodium amalgam gave monomeric **21** (Scheme 7). The formation of this terminal phosphide, which shows a chemical shift in the ^{31}P NMR spectrum of δ = 1010 ppm, was supported by an X-ray crystal structure that confirmed its anion–cation separation. Reaction with main-group halides

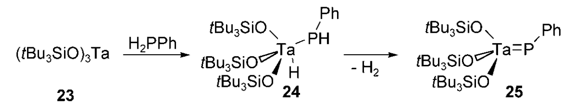


Scheme 7. Niobium phosphinidenes generated by P_4 activation.

resulted in niobium phosphinidene complexes [(ArNpN)$_3$Nb=P–R] (**22**; R = SiMe$_3$, SnMe$_3$, PPh$_2$, PtBu$_2$).[29b] The X-ray crystal structure for the SnMe$_3$ derivative reveals an elongated Nb=P bond (2.2731(8) Å) and a P–Sn single bond with a length (2.4778(8) Å) that matches the sum of the covalent radii of phosphorus and tin. The ^{31}P NMR spectral resonances ($\delta = 401.3$–607.0 ppm) of the niobium complexes **22** are in accord with a bent phosphinidene. Recently, Cummins and Cossairt also accomplished the synthesis of a diniobium octaphosphorus complex that contains a reactive phosphinophosphinidene moiety that was exploited for metathetical scission of the Nb=P bond.[30]

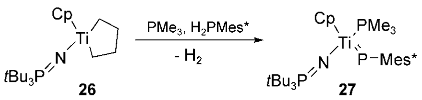
3.2. Insertion and Elimination

Inserting an electron-deficient organometallic fragment into a P–H bond is an alternative route to phosphinidene complexes. Oxidative addition of sterically unhindered phenylphosphine to the "electron-poor" tris(siloxy) tantalum complex **23** reportedly gives intermediate phosphide **24** and on 1,2-H$_2$ elimination tantalum phosphinidene complex [(tBu$_3$SiO)$_3$Ta=P–Ph] (**25**, Scheme 8).[31] The large siloxy groups ensure kinetic stabilization of the bent phosphinidene. Its X-ray crystal structure shows a short Ta=P bond of 2.317(4) Å and a bent Ta-P-Ph moiety (110.2(4)°). The preference of a bent over a linear phosphinidene complex was suggested to originate from an additional O(pπ)–Ta(dπ) donor interaction, which prevents the formation of an otherwise more favorable P(pπ)–Ta(dπ) interaction.



Scheme 8. Tantalum phosphinidene formed by P–H bond cleavage and subsequent 1,2-H$_2$ elimination.

In situ generation of a transient organometallic precursor is also a viable option. For example, compound **26** undergoes reductive elimination and reacts with one equivalent of the primary phosphine Mes*PH$_2$ in the presence of a threefold excess of PMe$_3$ to afford the isolable **27** (Scheme 9).[32]

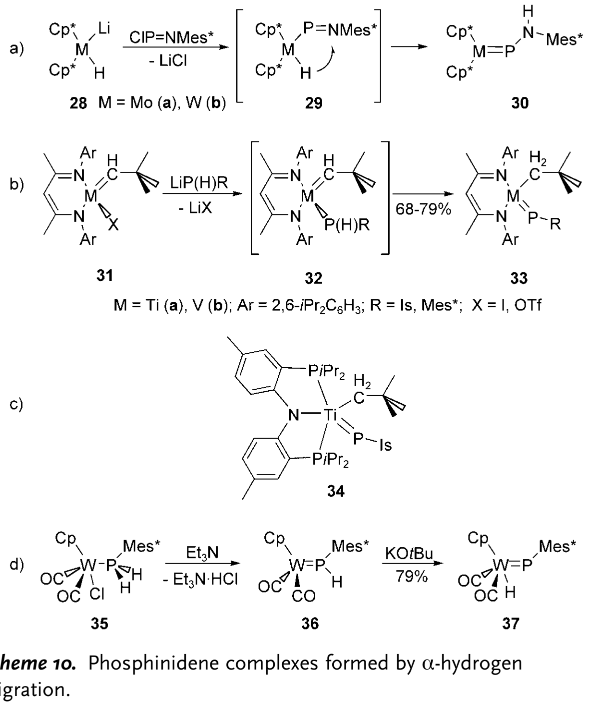


Scheme 9. Titanium phosphinidene formed by reductive elimination.

Although the structure of **27** could not be confirmed crystallographically, its resonances at $\delta = 769.9$, 35.3, and -10.3 ppm in the ^{31}P NMR spectrum are indicative of the terminal titanium phosphinidene fragment, the phosphinimide ligand, and the coordinated PMe$_3$, respectively. Additional ^{1}H and ^{13}C{^{1}H} NMR spectra were consistent with this formulation.

3.3. α-Hydrogen Migration

α-Hydrogen migration of the initial salt-metathesis product is another route to phosphinidene complexes. The first spectroscopic evidence for such a process was reported by Niecke et al. for amine-substituted complexes [Cp*$_2$M=P–N(H)Mes*] (**30a**,**b**, M = Mo (**a**), W (**b**); Scheme 10a),[33] which are similar to the complexes [Cp$_2$M=P–Mes*] (**1a**,**b**) reported by Lappert and co-workers.[12] Reaction of metal hydride **28a**,**b** with chloroiminophosphine ClP=NMes* is believed to give intermediate **29**, on the basis of the observed resonance at $\delta = 754$ ppm in the ^{31}P NMR spectrum at −40 °C for the tungsten complex. Above this temperature the metal hydride presumably undergoes a 1,3-hydrogen shift to yield



Scheme 10. Phosphinidene complexes formed by α-hydrogen migration.

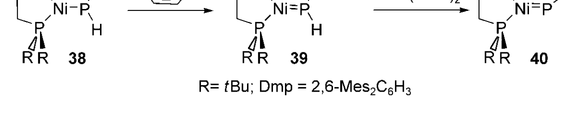
phosphinidene complex **30**, which was characterized by ^{31}P NMR spectroscopy (Mo $\delta = 770$ ppm, W $\delta = 663$ ppm) but could not be isolated.

A 1,3-shift of an α-hydrogen atom was used by Mindiola and co-workers to prepare the titanium and vanadium phosphinidene complexes $[(\text{nacnac})(\text{CH}_2t\text{Bu})\text{M}{=}\text{P}{-}\text{R}]$ (**33a**,**b**, M = Ti (**a**), V (**b**), nacnac = ArNC(Me)CHC(Me)-NAr; Scheme 10b). Salt metathesis of titanium alkylidene **31a** with LiPHR (R = Cy, Is, Mes*) at low temperature gave putative neopentylidene phosphide **32a**, which underwent α-hydrogen migration to give phosphinidene $[(\text{nacnac})(\text{CH}_2t\text{Bu})\text{Ti}{=}\text{P}{-}\text{R}]$ (**33a**, Scheme 10b).[34a] The Mes* derivatives has a short Ti≡P pseudo-triple bond (2.1831(4) Å) and a pseudo-linear Ti-P-Mes* unit (164.44(5)°),[34b] while solution spectra reveal two resonances in the ^{31}P NMR spectrum ($\delta =$ 242 and 216 ppm), suggesting the presence of two conformers.[34a] Paramagnetic vanadium complexes $[(\text{nacnac})(\text{CH}_2t\text{Bu})\text{V}{=}\text{P}{-}\text{R}]$ (**33b**, R = Is, Mes*) were synthesized analogously (Scheme 10b).[34c] The X-ray crystal structures reveal a distorted tetrahedral geometry at vanadium, a V=PR bond (Is 2.174(4) Å, Mes* 2.1602(6) Å) that is considerably shorter than those for the four-coordinate vanadium phosphides, and a V-P-C$_{ipso}$ angle that depends on the substituent at phosphorus (Is 136.6(5)°, Mes* 153.28(6)°). The generality of the α-hydrogen migration[28] was further demonstrated by the synthesis of titanium(IV) phosphinidene **34** (Scheme 10c), which bears the PNP-pincer ligand $\text{N}[2\text{-P-}(\text{CHMe}_2)_2\text{-4-methylphenyl}]_2^-$; imide and alkylidene functionalities can be obtained by the same approach.[34d]

Spectroscopic evidence for a base-induced 1,2-hydrogen shift leading to a phosphinidene complex was provided by Malish et al. (Scheme 10d).[35] Dehydrohalogenation of phosphine complex **35** with triethylamine gave phosphide complex **36**, which underwent a 1,2-H shift in the presence of KO*t*Bu, likely by a deprotonation–reprotonation sequence, to yield the evidently preferred phosphinidene complex $[\text{Cp}(\text{CO})_2\text{HW}{=}\text{P}{-}\text{Mes*}]$ (**37**). Whereas this product eluded isolation, it was characterized by its chemical shift at $\delta =$ 819.9 ppm ($^1J_{\text{PW}} = 123$ Hz) in the ^{31}P NMR spectrum and a hydride signal in the ^{1}H NMR spectrum at $\delta = -10.03$ ppm.

3.4. Oxidation and Deprotonation

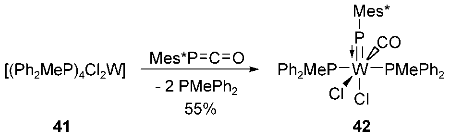
One-electron oxidation of paramagnetic nickel(I) phosphido complex **38** using tropylium hexafluorophosphate was shown by Hillhouse et al. to give cationic complex **39**, which can be deprotonated with a strong base to afford nickel(II) phosphinidene complex $[(\text{dtbpe})\text{Ni}{=}\text{P}{-}\text{Dmp}]$ (**40**, dtbpe = 1,2-bis(di-*tert*-butyl-phosphino)ethane; Scheme 11).[36] The structure has a short Ni=P bond of 2.0772(9) Å and a bent Ni-P-C unit with an angle of 130.78°, which is also reflected by its resonance at $\delta = 970$ ppm ($^2J_{\text{PP}} = 134$ Hz) in the ^{31}P NMR spectrum.



Scheme 11. Nickel phosphinidene complex formed by an oxidation–deprotonation sequence. TMS = Me$_3$Si.

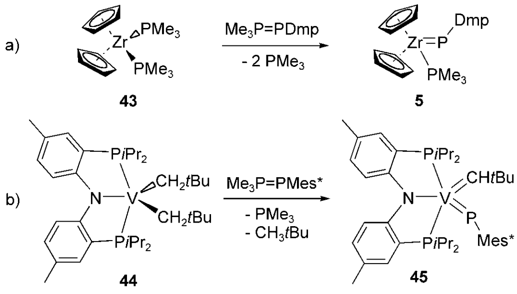
3.5. Phosphinidene Group Transfer

Phosphinidene complexes can also be prepared by RP group transfer using RP=X (X = CO, CNPh, PMe$_3$) as reagent. Cowley et al.[37] prepared tungsten phosphinidene $[(\text{MePh}_2\text{P})_2\text{Cl}_2\text{W}(\text{CO}){\equiv}\text{P}{-}\text{Mes*}]$ (**42**) by treating the 16-electron tetraphosphine complex $[(\text{MePh}_2\text{P})_4\text{Cl}_2\text{W}]$ (**41**) with phosphaketene Mes*P=C=O under elimination of two equivalents of phosphine (Scheme 12). In the phosphinidene product, the ketene's RP (axial) and CO (equatorial) moieties end up in a *syn* fashion, but the mechanism of formation is not known. The short W≡P separation of 2.169(1) Å suggests triple bonding. The large W-P-Mes* angle of 168.2(2)° is also reflected in the upfield chemical shift of $\delta = 193.0$ ppm in the ^{31}P NMR spectrum. The similar reaction with Mes*P=C=N−Ph likely gives the thermally unstable complex $[(\text{MePh}_2\text{P})_2\text{Cl}_2\text{W}(\text{C}{=}\text{N}{-}\text{Ph}){\equiv}\text{P}{-}\text{Mes*}]$.



Scheme 12. Tungsten phosphinidene **42** by phosphinidene group transfer.

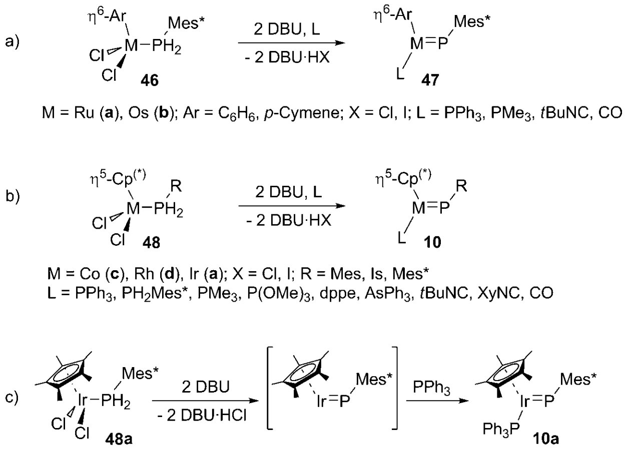
The groups of Mindiola and Protasiewicz jointly demonstrated that phospha-Wittig reagents of the type Me$_3$P=PAr are effective as PAr transfer reagents for the synthesis of stable phosphinidene complexes.[38] The phosphanylidene-σ^4-phosphorane reagents Me$_3$P=PAr (Ar = Mes*, Dmp) can deliver PAr fragments to low-valent early-transition-metal complexes **43** and **44** to effect oxidation to form terminal Zr$^{\text{IV}}$ phosphinidene **5** (Scheme 13a) and terminal V$^{\text{V}}$ phosphinidene **45** (Scheme 13b), respectively.



Scheme 13. Phosphinidene group transfer with phospha-Wittig reagents.

3.6. Dehydrohalogenation and Ligation

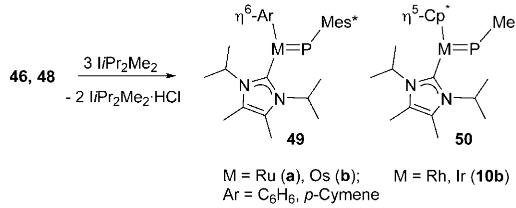
Base-induced double dehydrohalogenation of appropriate precursors in the presence of a suitable donor ligand was used by Lammertsma and co-workers to synthesize various Group 8 and 9 phosphinidene complexes in a one-pot procedure (Scheme 14 a,b). Illustrative is the formation of iridium phosphinidene complex [Cp*(Ph_3P)Ir=P–Mes*] (**10 a**) by dehydrohalogenation of phosphine complex **48 a** with two equivalents of 1,8-biazabicyclo-[5.4.0]-undec-7-ene (DBU) and capture of the putative 16-electron complex [Cp*Ir=P–Mes*] by the donor ligand PPh_3 (Scheme 14 c).[25a] This mild procedure proved equally effective for various other donor ligands L (PH_2Mes*, PMe_3, $P(OMe)_3$, dppe, $AsPh_3$, *t*BuNC, XyNC, CO; Scheme 14 a).[25a] The X-ray crystal structure of the CO-ligated complex [Cp*(CO)Ir=P–Mes*] (Ir=P 2.1783(8) Å, Ir-P-Mes* 113.77(10)°) shows a *Z* conformation for the double bond, which is attributed to the small size of the CO ligand and differs from that of the PPh_3-ligated complex, which has an *E* conformation but otherwise similar structural features. The deshielded resonance in the ^{31}P NMR spectrum for the CO-ligated complex ($\delta = 805$ ppm), as compared to the phosphane analogue ($\delta = 687$ ppm), was attributed to the CO π-acceptor capabilities rather than to geometrical differences.[25] The X-ray crystal structure for the only isolable cobalt phosphinidene complex [Cp(Ph_3P)Co=P–Mes*] (**10 c**) shows a piano-stool geometry with bonding properties (Co=P 2.1102(8) Å, Co-P-Mes* 109.00(9)°) that closely resemble iridium analogue **10 a**.[39] The CO-ligated Co complex *Z*-[Cp(CO)Co=P–Mes*] was identified by its characteristic low-field resonance in the ^{31}P NMR spectrum at $\delta = 1047$ ppm.



Scheme 14. Dehydrohalogenation/ligation for a) Group 8 and b) Group 9 transition-metal phosphinidene complexes. c) Synthesis of phosphinidene complex **10 a** via putative [Cp*Ir=P–Mes*] from iridium precursor **48 a**. dppe = 1,2-bis(diphenylphosphino)ethane, Xy = xylyl.

Illustrative for Group 8 phosphinidenes are the ruthenium complexes [η^6-Ar(L)Ru=P–Mes*] (**47 a**, Ar = benzene, *p*-cymene; L = PPh_3, PMe_3, *t*BuNC; Scheme 14 a) with resonances in the ^{31}P NMR spectra in the range $\delta = 801$–846 ppm, while the non-isolable CO-ligated complex [η^6-C_6H_6(CO)Ru=P–Mes*] reportedly has a chemical shift at lower field ($\delta = 897$ ppm).[40] Ruthenium phosphinidenes [η^6-*p*Cym(R_3P)Ru=P-Mes*] **47 a** (R = Ph, Cy) are also accessible from [η^6-*p*Cym$RuCl_2(PR_3)$] by reaction with DBU and PH_2Mes*.[41] The heavier osmium phosphinidene complexes [η^6-Ar(L)Os=P–Mes*] (**47 b**, Ar = benzene, *p*-cymene; L = PPh_3, PMe_3, CO) were obtained equally readily from dehydrohalogenation ligation of the primary complexed phosphine [η^6-Ar$OsX_2(PH_2$Mes*)] (**46 b**).[40] Similar to the third-row Group 9 transition metal iridium, the CO-ligated osmium complex [η^6-Ar(CO)Os=P–Mes*] (**47 b**) could also be isolated. The *E* isomers were shown to be favored for complexes having large PR substituents (e.g. Mes*) and bulky ligands (e.g. PPh_3), the *Z* isomer for the smaller carbon monoxide ligand, and a mixture of *E*/*Z* products for ligands of intermediate size, such as PMe_3 or $P(OMe)_3$.[25,39]

Dehydrohalogenation and ligation also proved an effective route to introduce N-heterocyclic carbene ligands, such as I*i*Pr_2Me_2.[42] For example, the one-pot reaction of ruthenium and osmium precursors **46 a**,**b** and rhodium and iridium precursors **48 a**,**b** with three equivalents of I*i*Pr_2Me_2 yielded the corresponding Group 8 and 9 NHC-ligated phosphinidene complexes **49**,**10 b** and **50 a**,**b**, respectively (Scheme 15).[43,44] Because the NHC is the stronger base (pK_a = 24.0 for I*i*Pr_2Me_2 in [D_6]DMSO),[45] DBU (pK_a = 11.3)[46] cannot be used for the dehydrohalogenation,[25a,39,40,47] thereby necessitating the use of two equivalents of NHC as base and one as stabilizing ligand. However, the carbene can be regenerated by deprotonation of the imidazolium salt I*i*Pr_2Me_2·HCl that precipitates.[48] The NHC-functionalized phosphinidene complexes were obtained as colored, air- and moisture- sensitive but thermally stable solids with characteristic resonances in the ^{31}P NMR spectra (Ir $\delta = 560.0$ ppm (**10 b**), Ru $\delta = 751.7$ ppm (**49 a**), Os $\delta = 557.6$ ppm (**49 b**), Rh $\delta = 745.9$ ppm (**50**)) that reflect shielding arising from the σ-donor capacity of the NHC ligand. The X-ray crystal structure of rhodium complex [η^5-Cp*(I*i*Pr_2Me_2)Rh=P–Mes*] (**50**) shows a Rh=P bond length of 2.1827(7) Å and a Rh-P-Mes* angle of 107.65(4)°, which are similar to those for iridium complex **10 b** and ruthenium complex [(η^6-C_6H_6)(I*i*Pr_2Me_2)Ru=P–Mes*] (**49 a**, Ru=P 2.2222(8) Å, Ru-P-Mes* 105.82(10)°). Both phosphinidene complexes have pronounced M–C single bonds with lengths of 2.036(2) (Rh) and 2.091(3) Å (Ru) that are in the typical range for M–NHC complexes.[49]



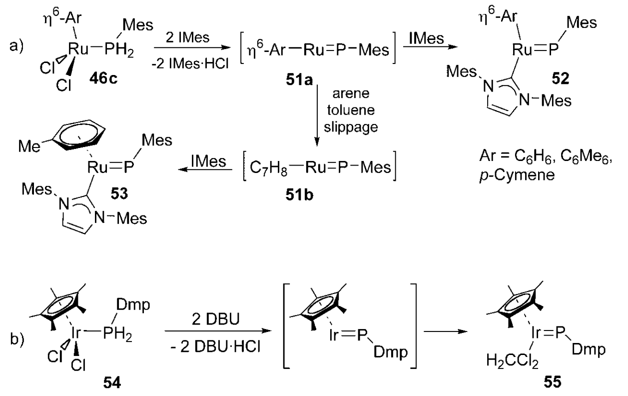
Scheme 15. Dehydrohalogenation and ligation using NHCs.

4. Reactivity of Nucleophilic Phosphinidene Complexes

To review the reactivities of the nucleophilic, 18-electron phosphinidene complexes it is relevant to recognize the impact of the putative 16-electron [LM=P−R] species. Although their involvement in the reactions often cannot be ascertained, they are evolving as reactive entities that we address separately.

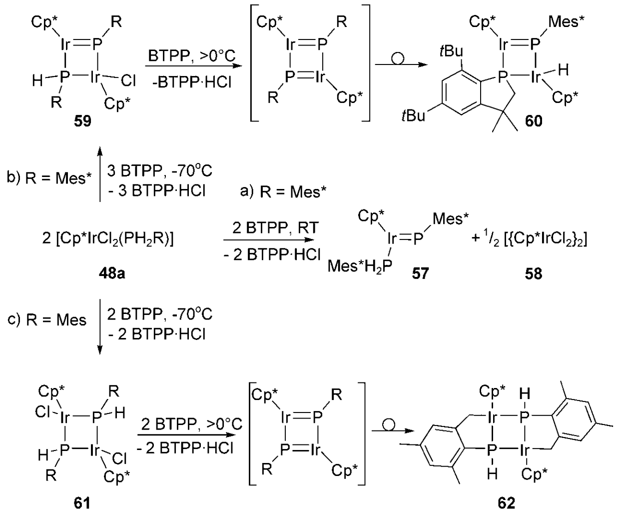
4.1. Reactive 16-Electron Intermediates

Convincing spectroscopic evidence has been presented for the reactive, 16-electron intermediates [LM=P−Mes*] (L = η^5-Cp$^{(*)}$, η^6-Ar). They presumably form in situ on dehydrohalogenation of primary phosphine complexes, such as **46** and **48**, and are than captured by a ligand to give the discussed 18-electron phosphinidene complexes. Slowing down the ligation by using the heavily congested carbene IMes (1,3-dimesitylimidazol-2-ylidene)[43,44] both as base and as ligand in the reaction with [η^6-*p*CymRuCl$_2$(PH$_2$Mes)] (**46c**) gave the expected phosphinidene complex **52** as well as isomer **53**, in which the *p*-cymene group is replaced by a toluene solvent molecule, thus indicating the conversion of the 16-electron intermediate [η^6-*p*CymRu=P−Mes] (**51a**) to [η^6-TolRu=P−Mes] (**51b**, Scheme 16a).



Scheme 16. Solvent-stabilized phosphinidene complexes.

Solvent stabilization was demonstrated for the putative 16-electron complex carrying the bulky phosphorus substituent 2,6-dimesitylphenyl (Dmp). Monitoring the reaction of **54** with DBU in dichloromethane by ^{31}P NMR spectroscopy showed the appearance of a characteristic low-field resonance at $\delta = 672$ ppm, which concurs with the $\delta = 684$ ppm calculated at the BP86/TZP level of theory for dichloromethane-solvated phosphinidene **55** (Scheme 16b).[50] Hey-Hawkins and co-workers reported that, in the absence of a stabilizing donor ligand, on dehydrohalogenation of tantalum-complexed primary phosphine [Cp*(Cl$_4$)Ta(PH$_2$−Is)], the 14-electron phosphinidene complex [Cp*(Cl$_2$)Ta=P−Is] (**56**, ^{31}P $\delta = 488.0$ ppm) was isolated; no mention was made of intermediate products.[51]

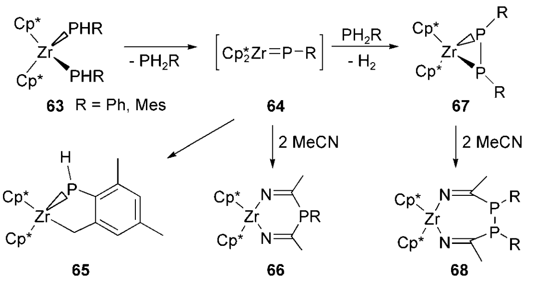


Scheme 17. Dehydrohalogenation in the absence of a stabilizing ligand.

Lammertsma and co-workers showed that dehydrohalogenation of primary phosphine complex **48a** with the strong phosphazene base *tert*-butylimino-tri(pyrrolidino)phosphorane (BTPP, p$K_b \approx 26$) in the absence of a ligand gave 18-electron complex **57** and one-half equivalent of the dimer [{Cp*IrCl$_2$}$_2$] (**58**, Scheme 17a).[52] Phosphinidene **57** was interpreted to result from [Cp*Ir=P−Mes*] abstracting PH$_2$Mes* from its precursor. Reaction at low temperature showed the intermediate formation of **59** (Scheme 17b), which results from [2+2]-cycloaddition of [Cp*Ir=P−Mes*] and [Cp*(Cl)Ir=P(H)Mes*], as identified by its ^{31}P NMR spectrum ($\delta = 366$ and -126 ppm), and suggests that the first dehydrohalogenation is faster than the second one. The reaction appears to be sensitive to the size of the substituent on phosphorus, as the smaller Mes group gave the intermediate dimetallacycle **61**, resulting from dimerization of [Cp*(Cl)Ir=P(H)Mes], and subsequently on dehydrohalogenation dimer **62** (Scheme 17c).

Stephan and co-workers reported on the generation and reactivity of the transient, 16-electron phosphinidene [Cp*$_2$Zr=P−R] (**64**),[19] which can be generated from primary phosphide complex **63** by elimination of phosphane H$_2$PR (Scheme 18). Attempts to isolate **64** were unsuccessful. However, it could be detected by ^{31}P NMR spectroscopy at $\delta = 537$ ppm as an unstable [Cp*$_2$Zr=P−Mes]·LiCl adduct when prepared from [Cp*$_2$ZrCl$_2$] and LiPHMes in dimethoxyethane (DME).[19a,b] In situ generated **64** (R = Mes) is highly reactive and gives **65** by intramolecular C−H insertion and yields metallacycle **66** by reaction with acetonitrile (Scheme 18).[19] The reinsertion of phosphane H$_2$PR into the Zr=P bond of **64** is also feasible and yields complex **67** (and **68** upon reaction with MeCN) irreversibly with elimination of H$_2$ as the driving force (Scheme 18).[19]

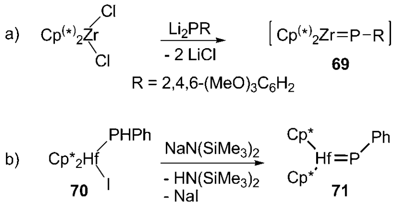
Stephan and co-workers reported other examples of the transient 16-electron [Cp$^{(*)}_2$Zr=P−R] (R = SiPh$_3$ $\delta = 263$,



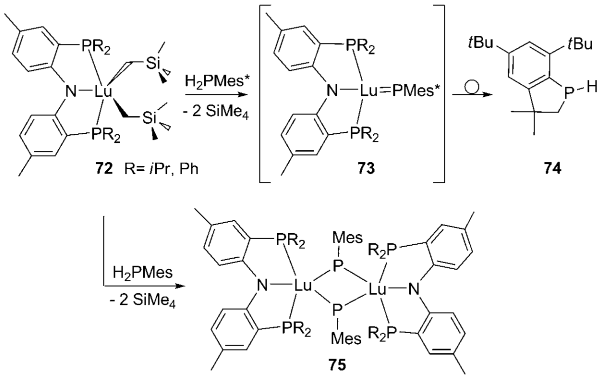
Scheme 18. Formation and reactivity of [Cp*$_2$Zr=P–R].

Mes* 478, Cy 499, Mes 526, Ph 579 ppm), all of which were characterized by their ^{31}P NMR spectra.[19,20]

Majoral and co-workers reported chemical shifts in the ^{31}P NMR spectra for [Cp$^{(*)}_2$Zr=P–(2,4,6-(MeO)$_3$C$_6$H$_2$)] (**69a**,**b**, Cp $\delta = 465$, Cp* 438 ppm) using the salt metathesis approach (Scheme 19a), but dimers and polymeric forms could not be excluded.[53] The heavier hafnium congener [Cp*$_2$Hf=P–Ph] (**71**) was postulated to be formed from the reaction of precursor **70** with NaN(SiMe$_3$)$_2$ as base (Scheme 19b), on the basis of its ^{31}P resonance at $\delta = 376$ ppm, but it was not isolated or trapped.[54] Attempts to kinetically stabilize the transient lanthanide phosphinidene complex **73** that was generated from **72** by employing the bulky phosphine H$_2$PMes* resulted in C–H activation and formation of phosphaindole **74** (Scheme 20). The sterically less hindered H$_2$PMes was shown to give isolable lutetium dimer **75**, presumably by dimerization of the putative monomeric complex.[55]



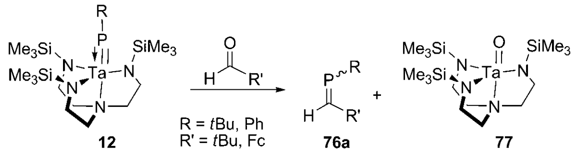
Scheme 19. Formation of transient Zr and Hf phosphinidenes.



Scheme 20. Postulated lanthanide phosphinidene **73** and isolable Lu dimer **75**.

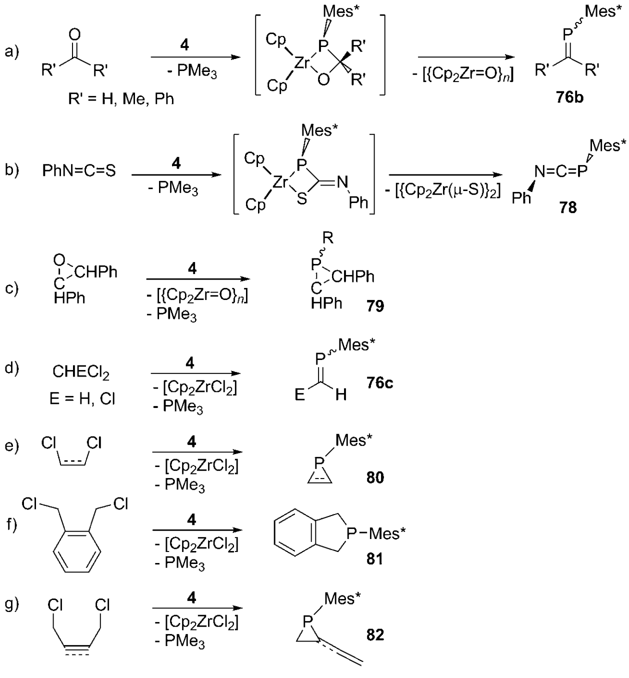
4.2. R–P Transfer

Schrock and co-workers were the first to report on the phospha-Wittig reactivity of nucleophilic phosphinidenes by showing that tantalum complex **12** reacts with carbonyl compounds to yield phosphaalkene **76a** and Ta=O complex **77** (Scheme 21).[26] As Schrock also showed in earlier work[56] that Ta alkylidenes and carbonyl compounds yield alkenes and Ta=O species, the P/C analogy between phosphinidene and carbene complexes is demonstrated.



Scheme 21. Phosphinidene transfer reaction of tantalum complex **12**. Fc = ferrocenyl.

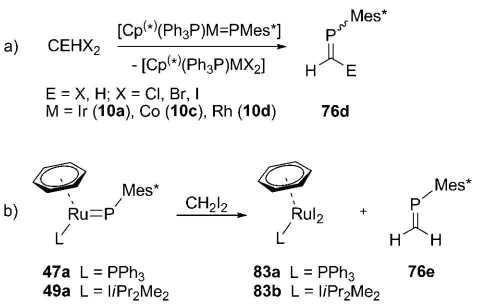
Of all the 18-electron phosphinidene complexes, Zr phosphinidene **4** developed by Stephan is the most extensively studied, and a variety of phosphinidene transfer reactions has been developed.[7] The phospha-Wittig reaction that transfers a PR group is the most widely applied reaction of nucleophilic phosphinidene complexes of oxo- or halophilic transition metals such as Zr (Scheme 22). Stephan and co-workers demonstrated that the reaction of zirconium complex **4** with ketones and aldehydes yields phosphaalkenes **76b** and the insoluble zirconocene oxide [{Cp$_2$ZrO}$_n$], which is easily separated from the product, together with uncoordinated PMe$_3$ (Scheme 22a).[20b]



Scheme 22. Phosphinidene transfer reactions of phosphinidene **4**.

This metathesis reaction is thought to proceed by initial decoordination of PMe$_3$, thus generating the active 16-electron species [Cp$_2$Zr=P–Mes*]. Subsequent coordination of the carbonyl species to Zr followed by intramolecular attack of the nucleophilic phosphorus atom gives a four-membered-ring intermediate (Scheme 22 a), which by retrocyclization yields the P=C and Zr=O products. Phosphinidene **4** also undergoes a metathesis reaction with phenylisothiocyanate to give heteroallene *E*-PhN=C=PMes* **78** and the insoluble zirconocene sulfide dimer [{Cp$_2$Zr(μ-S)}$_2$] (Scheme 22 b).[20b] Furthermore, epoxides can be converted into the three-membered-ring phosphiranes **79** by P/O exchange (Scheme 22 c),[20b] whereas **4** in the presence of *gem*-dihalides and CHCl$_3$ affords phosphaalkene **76c** (Scheme 22 d).[20b] This approach was successfully extended to the synthesis of phosphirene **80**, phospholane **81**, and the substituted phosphirane **82** (Scheme 22 e,f,g).[20b] The mechanism for formation of phosphirane **80** from Zr phosphinidene **4** and 1,2-dichloroethane, invoking the 16-electron complex [Cp$_2$Zr=P–Mes*], was also addressed computationally.[57]

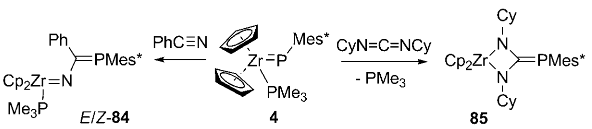
Lammertsma and co-workers showed that the rate of the reaction of phosphinidenes **10** (M = Co (**10c**), Rh (**10d**), Ir (**10a**)) with dihalomethanes to afford phosphaalkene **76d** (Scheme 23 a) depends on the halogen atom of the substrate, the oxo- and halophilicity of the transition metal, and the electronic properties of the ancillary ligand.[25a,39,43,44] The influence of the stabilizing ligand was demonstrated by exchanging the phosphane donor of complex **47a** (L = PPh$_3$) for a NHC ligand in **49a** (I*i*Pr$_2$Me$_2$), which accelerates (by 40 times) the formation H$_2$C=PMes* (**76e**, Scheme 23 b).[43] It was demonstrated that for **49a**, the relative σ-donor/π-acceptor ability of the NHC ligands can easily be influenced by a simple substituent-controlled conformational change.[43]



Scheme 23. Phosphinidene transfer reactions of late-transition-metal phosphinidenes.

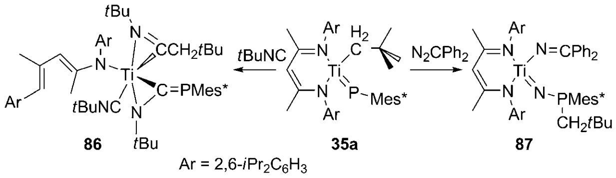
4.3. Insertion into the M=P Bond

The groups of Stephan and Mindiola reported on the insertion of substrate molecules into the M=P bond. For example, whereas reaction of Zr complex **4** with PhCN afforded *E*/*Z* imido complex **84** in a 1:1 ratio (Scheme 24),[20b] that with dicyclohexylcarbodiimide gave insertion into the Zr=PMes* bond to yield the X-ray crystallographically characterized phosphaguanidino complex **85** (Scheme 24).[20b]



Scheme 24. Zr=P bond insertion reactions.

The coordinatively unsaturated titanium phosphinidene complex **35a** reacts with *t*BuNC to afford the rare η^2-(N,C)-phosphaazaallene complex **86** (Scheme 25).[34b] The two resonances in the ^{31}P NMR spectrum at $\delta = -8.5$ and -17.6 ppm for **86** indicate the presence of two isomers in solution. Reaction of **35a** with N$_2$CPh$_2$ yielded complex **87**, which contains an uncommon phosphinylimide ligand.[34b] Both complexes (**86** and **87**) are exceedingly reactive and readily decompose in solution and in the solid state.

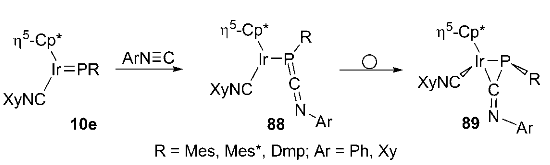


Scheme 25. Insertion reactions into the Ti=P bond.

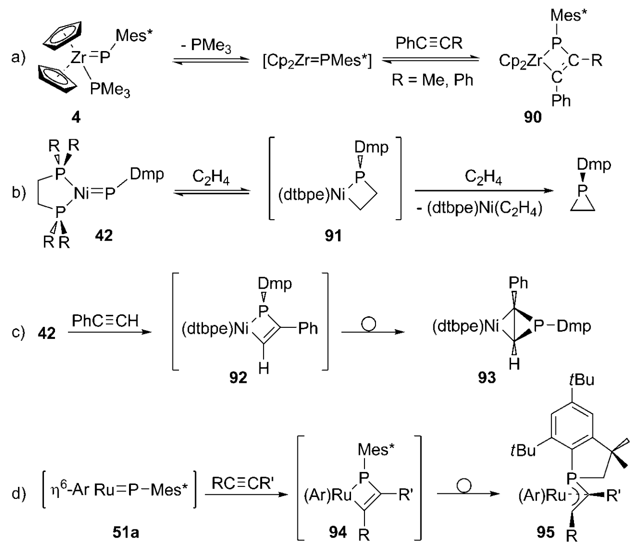
4.4. Cycloaddition to the M=P Bond

[1+2]- and [2+2]-(retro)cycloadditions are important metal-assisted bond-forming and bond-breaking reactions that are well-established for metal alkylidenes,[58] in contrast to the nucleophilic phosphinidene complexes. Only a few examples have been reported, such as the stepwise addition of isocyanides. In situ generated 16-electron complex [Cp*Ir=P–R] (R = Mes, Mes*, Dmp) was shown to react with an isocyanide to form 18-electron phosphinidene complex [Cp*(XyNC)Ir=P–R] (**10e**). Subsequent reaction with ArNC (Ar = Ph, Xy) gave complex **89**, presumably via intermediate **88**, as indicated by DFT calculations (Scheme 26).[50]

An example of the [2+2]-cycloaddition of C=C and C≡C multiple bonds to metal phosphinidenes was provided by Stephan and Breen. Zirconium complex **4** reversibly adds to acetylenes to afford phosphametallacycle **90**, which has an indicative resonance at $\delta = 55$ ppm in the ^{31}P NMR spectrum (Scheme 27 a).[59] Loss of PMe$_3$ from **4** is the rate-determining step in this reaction. It was shown that a more expeditious



Scheme 26. [1+2]-cycloaddition of phosphinidene and isocyanide.



Ar = C_6H_6, *p*-Cymene; R = Me, Ph, $SiMe_3$; R' = H, Me

Scheme 27. [2+2] cycloaddition reactions.

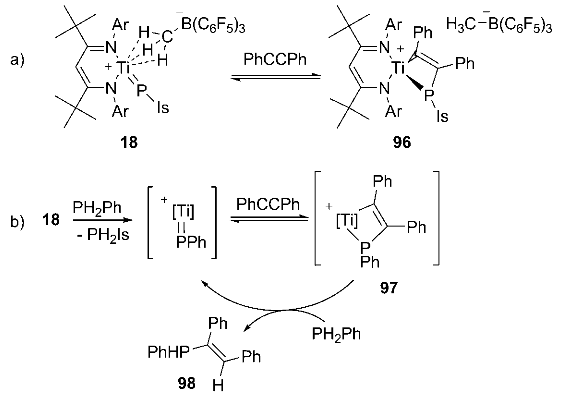
version of this reaction starts with the spontaneous loss of methane from $[Cp_2(Me)ZrPH{-}Mes^*]$.[59]

Hillhouse and Waterman showed that nickel phosphinidene **42** reacts with olefins to form phosphirane *cyclo*-C_2H_4PDmp in a stereoselective manner by way of metallacyclobutane **91** (Scheme 27b).[60] Moreover, **42** was shown to undergo cycloaddition with alkynes to give the putative [2+2]-adduct phosphametallacyclobutene **92**, which rearranges to the more stable metallaphosphabicyclobutane **93** (Scheme 27c).[61]

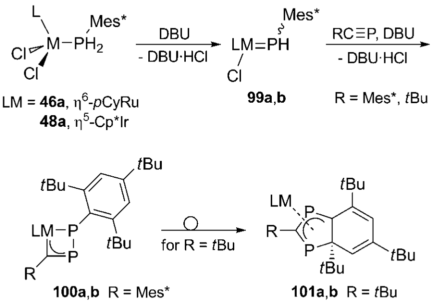
Ruthenium phosphinidenes **51a** generated in situ also react with alkynes, as shown by Lammertsma and co-workers,[40] to give the stable phosphaallyl complexes **95** (Scheme 27d). It was reasoned that first [2+2]-cycloadduct **94** is formed, which subsequently undergoes C–H activation to yield the final product. Analogously, Menye-Biyogo et al. have reported the formation of the putative phosphinidenes **51a** from the interaction of phosphinidene complex $[\eta^6\text{-}p\mathrm{Cym}(Cy_3P)Ru{=}P{-}Mes^*]$ and alkynes by loss of the phosphine ligand.[62]

Zwitterionic titanium phosphinidene **18** with its labile borate group was shown to undergo [2+2]-cycloaddition with diphenylacetylene to generate phosphatitanocyclobutene **96** (Scheme 28a),[28] which was identified on the basis of its characteristic chemical shifts in the ^{31}P ($\delta = 160.7$ ppm) and ^{13}C NMR spectra ($\delta = 253.5$ ppm). Complex **18** was demonstrated to be able to function as a precatalyst in the catalytic hydrophosphination of PhCCPh with $PhPH_2$. The proposed mechanism (Scheme 28b) involves PAr transfer of the primary phosphine and subsequent [2+2]-cycloaddition of diphenylacetylene to form **97**, which generates vinylphosphine $PhHP(Ph)C{=}CHPh$ **98** upon reaction with phenylphosphine.[28]

A diphosphorus analogue of the versatile Dötz intermediate that is common in the chemistry of complexed carbenes has been reported by the group of Lammertsma. η^3-Diphosphavinylcarbene complex **100** resulted on the DBU-induced reaction of Ru- and Ir-complexed primary phosphines **46a** and **48a** with phosphaalkyne $Mes^*C{\equiv}P$ (Scheme 29).[63] The product obtained with the less congested



Scheme 28. a) [2+2]-cycloaddition reaction and b) proposed catalytic PAr transfer in hydrophosphination reactions for Ti phosphinidene **18**. The β-diketiminate ligand and the $BCH_3(C_6F_5)_3$ anion in (b) are omitted for clarity.



Scheme 29. Synthesis and rearrangement of η^3-diphosphavinylcarbene **100**.

$tBuC{\equiv}P$ was shown to convert to the 1,3-diphospha-3*H*-indene complex **101**, which resembles the intermediate of the Dötz benzannulation reaction (Scheme 29).[63] The reversibility of the phosphaalkyne addition was demonstrated by the exchange of $Mes^*C{\equiv}P$ in **100b** with PPh_3 and $tBuC{\equiv}P$, yielding phosphinidene complex **47a** and **101b**, respectively.[63]

5. Conclusion

The emerging applicability of terminal phosphinidene complexes that are nucleophilic at the phosphorus atom drives the search for novel reagents and new reactions. The past decades have shown many openings to further develop this chemistry. Whereas the focus was initially on stable 18-electron complexes, it is evident that the in situ generated 16-electron analogues are viable reactive intermediates. Much ground still needs to be covered, but it is clear that the broad spectrum of reactions that are commonplace for transition-metal-complexed carbenes are also feasible for the phosphinidenes, such as [2+2]-cycloadditions to C–C multiple bonds, insertions into single bonds, and phospha-Wittig type reactions. Moreover, the diagonal relationship between phosphorus and carbon in the Periodic Table provides opportunities to mimic the carbene complexes by conducting mechanistic studies that take advantage of the stabilizing phosphorus atom. Exemplary is the diphospha-Dötz intermediate. There are many more possibilities. With the increasing emphasis on the element phosphorus in conducting organic conversions, in ligands and catalysts, and in the advance of metal-assisted organophosphorus chemistry, much can be expected from this field.

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