ORGANOMETALLICS

Ambiphilic Reactivity of a Ruthenaphosphaalkenyl: Synthesis of *P*-Pyrazolylphosphaalkene Complexes of Ruthenium(0)

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Supporting Information

ABSTRACT: The novel ruthenaphosphaalkenyl complex $[Ru{P=CH(SiMe_3)}Cl(CO)(PPh_3)_2]$, prepared from $[RuHCl(CO)(PPh_3)_3]$ and $Me_3SiC\equiv P$, exhibits ambiphilic behavior, reacting at phosphorus with both nucleophiles and electrophiles. Its reaction with Li(pz') or $K[HB(pz')_3]$ (pz' = pz, pz^*) affords $[Ru{\eta^1-N:\eta^2-P,C-P(pz')=CH(SiMe_3)}(CO)(PPh_3)_2]$, a rare example of a ruthenium(0) η^2 -phosphaalkene complex and the first example of a *P*-pyrazolylphosphaalkene. Conversely, reaction with the electrophilic PhHgCl leads to metalation at phosphorus, affording $[Ru{\eta^1-P(HgPh)=CH(SiMe_3)}Cl_2(CO)(PPh_3)_2]$.

PhHgCl OSC, PPh3 H Ru-P SIMe3 PZ Cl PPh3 PPh3 Cl PPh3

The chemistry of low-coordinate phosphorus¹ continues to develop, with an ever-increasing focus on organometallic systems;² among these, interest in the metallaphosphaalkenes, which embody at least one metal substituent on the "P=C" unit, has grown with notable rapidity.^{3,4} Within this class of compounds, particularly intriguing are the *P*-metallaphosphaalkenes (M-P=CRR'; Chart 1). First described in 1985⁵ and

Chart 1. Representative I	P-Metallapho	osphaalkenyls
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$\begin{array}{cc} Cp'_{A} & Cp'_{A} \\ OC^{M}_{P} \xrightarrow{CO} R' & OC^{Fe}_{P} \xrightarrow{Fe}_{P} \\ OC & R & OC \end{array}$, OC L H Ru-P R L CI	
Cp' = Cp, Cp*; M = Mo, W	$L = PPh_3$	
R' = SiMe ₃ ; R = SiMe ₃ , Ph	R = ^t Bu 1	
R' = OSiMe ₃ ; R = SiMe ₃ , Ph	ı, Ad 2	
^t Bu, Mes		

the subject of continued interest and study,^{6–8} these remain relatively rare. As with their organic counterparts, such compounds traditionally relied upon sterically encumbering or π -dative substituents (CR₂ = C(SiMe₃)₂, C(NMe₂)₂; CRR', R = SiMe₃, R' = Ph, R = OSiMe₃, R' = Mes, Ph, 'Bu) to confer stability; however, with Hill and Jones' report of [Ru(P= CHR)Cl(CO)(PPh₃)₂] (R = 'Bu (1),⁹ Ad (2)),¹⁰ obtained by hydroruthenation of the respective phosphaalkynes, access to monosubstituted and unencumbered *P*-metallaphosphaalkenes was finally established. Nonetheless, few further analogues have been reported.^{11–13}

Investigation of the chemistry of *P*-metallaphosphaalkenes has included demonstration of their cycloadditions with alkenes,¹⁴ alkynes,¹⁵ and azo and diazo compounds;^{16,17} additionally, the $P^{\delta-} = C^{\delta+}$ polarization achieved within *C*amino derivatives has been exploited in protonation and alkylation reactions.¹⁸ Significantly, comparable reactivity toward electrophilic species has been demonstrated for **1**, which is devoid of additional π -donor substituents. Thus, the electrophiles "EX" (MeI, AuCl(PPh₃) and RHgCl (R = Fc, Ph)) react with 1 to afford the respective η^1 -phosphaalkene complexes $[R_2C=P(E)\rightarrow RuCl(X)(PPh_3)_2(CO)]^{.19}$

As part of an extended investigation into unsaturated phosphacarbon complexes and their derivatization, we were interested in expanding the range of known *P*-metallaphosphaalkenyls and further exploring their chemistry. Herein, we report the synthesis of $[Ru\{P=CH(SiMe_3)\}Cl(CO)(PPh_3)_2]$ and its unprecedented ambiphilic nature, facilitating *P*functionalization by both electrophilic and nucleophilic reagents; the latter affords the first examples of *P*pyrazolylphosphaalkenes, which are held within the metal coordination sphere.

The novel ruthenaphosphaalkenyl compound $[Ru{P=CH-(SiMe_3)}Cl(CO)(PPh_3)_2]$ (3; Scheme 1) is conveniently





Reagents and conditions: (i) $[RuHCl(CO)(PPh_3)_3]$, $CH_2Cl_2/$ toluene, 2 h; (ii) Li(pz'), thf, 1 h.

prepared by a modification of Hill's method, from [RuHCl-(CO)(PPh₃)₃] and excess Me₃SiC \equiv P,^{20–22} as an air-sensitive yellow solid.²³ While **3** has not yet ceded to the growth of crystals, its identity follows from analytical and spectroscopic data.²⁴ These include a characteristic ³¹P NMR spectrum, which indicates retention of two PPh₃ ligands (d, $\delta_{\rm P}$ 34.6, $J_{\rm PP}$ = 8 Hz, 2P) and also exhibits a heavily deshielded resonance (dt, $\delta_{\rm P}$ 548.5, $J_{\rm PP}$ = 8 Hz, $J_{\rm PH}$ = 21 Hz, 1P), attributed to the

Received: March 11, 2013 Published: April 24, 2013 phosphaalkenyl center, which collapses to a triplet in the ${}^{31}P{}^{1}H$ NMR spectrum, consistent with loss of the scalar interaction to the vinylic CH proton. The latter is observed at 7.28 ppm in the ¹H NMR spectrum and identified on the basis of its correlation with the phosphorus (δ_{P} 548.5), carbon (δ_{C} 168.0), and silicon (δ_{Si} –9.40) centers of the phosphaalkenyl moiety. Retention of the carbonyl ligand is apparent from infrared data (ν_{CO} 1920 cm⁻¹), while the gross composition was verified by elemental analysis.

In THF solution, compound 3 reacts readily with the lithium pyrazolates Li(pz') ($pz' = pz^*$, pz) over 1 h to afford in each case high yields (>70%) of a single phosphorus-containing product (4 and 5, respectively), obtained in analytical purity by recrystallization from CH₂Cl₂.^{25,26} Both 4 and 5 exhibit characteristic ³¹P NMR spectra, which indicate loss of the phosphaalkenic center, its resonance apparently being replaced by one in the saturated region of the spectrum (60-30 ppm)that couples to each of the, now inequivalent, PPh₃ centers. Further salient spectroscopic data include (i) ¹H NMR resonances associated with a single pz' unit, integrating consistently against PPh3, (ii) appreciably shifted ¹H and ¹³C resonances associated with the P–CH unit (vide infra), (iii) ¹H and ²⁹Si signals indicative of the retained SiMe₃ group, and (iv) a single carbonyl stretching mode ($\nu_{\rm CO}$ 1900 cm⁻¹). The identities of 4 and 5 were ultimately established from X-ray diffraction studies, single crystals being obtained by slow cooling of saturated CH₂Cl₂ solutions. While the data for 4 are of low quality, they confirm connectivity comparable to that adopted by 5 (Scheme 1, Figure 1).²⁷



Figure 1. Molecular structure of **5** (50% thermal ellipsoids). The phenyl groups are reduced and hydrogen atoms omitted for clarity. The asymmetric unit contains two unique molecules of **5**; numbering of the second molecule (shown in the Supporting Information) is comparable (i.e., P11 vs P21). Selected bond lengths (Å) and angles (deg): P21-C21 = 1.793(6), P21-N21 = 1.809(5), Ru21-P21 = 2.377(2), Ru21-C21 = 2.215(6), Ru21-C22 = 1.835(5), Ru21-N22 = 2.190(4), C22-O21 = 1.154(6); P21-C21-Si21 = 116.7(3), P21-C21-H21 = 112.8, Si21-C21-H21 = 112.8.

The core geometry of **5** might reasonably be described as a ruthenaphosphirane, insofar as significant pyramidalization is noted at the C_{alkene} center ($\angle P-C-H = 112.8^{\circ}$, $\angle Si-C-H = 112.8^{\circ}$, $\angle P-C-Si = 116.7^{\circ}$), while the P–C linkage (1.793(6) Å; P11–C11 = 1.779(6) Å) is appreciably lengthened from those previously reported for phosphaalkenyls (1.65–1.75 Å).²⁸ This distance is, however, shorter than a typical P(sp³)–C(sp³) single bond (1.855(19) Å)²⁹ and, indeed, those of other

phosphiranes (1.8–1.9 Å). Moreover, while the acute angles about phosphorus (\angle Ru–P–C = 62.4°, \angle N–P–C = 94.4°, \angle N–P–Ru = 81.9°) might reasonably be attributed to the geometric constraints of the pyrazolyl bridge, those about carbon are more clearly indicative of a geometry intermediate between sp² and sp³, albeit that spectroscopic data ($\delta_{\rm C}$ 47.5; $\delta_{\rm H}$ 1.59, ${}^{1}J_{\rm CH} \approx$ 123 Hz; cf. CH₄ 125 Hz³⁰) more strongly support an sp³ model.

The ³¹P NMR data are not conclusively consistent with the ruthenaphosphirane model, since the intrinsic metal—phosphide linkage ought to induce appreciable deshielding of the phosphorus center, albeit that phosphiranes typically exhibit appreciably shielded phosphorus centers.^{31–33} The infrared data are more informative, suggesting a ruthenium(0) center ($\nu_{\rm CO} \sim 1900 \text{ cm}^{-1}$) rather than Ru(II).^{34–36} We thus reason that **5** is better formulated as an $\eta^1:\eta^2$ -coordinated *P*-pyrazolylphosphaalkene complex, the observed spectroscopic data reflecting a dominant contribution from $d_{\pi} \rightarrow \pi^*_{P=C}$ retro-donation in phosphaalkene binding.³⁷ Indeed, Cowley described a similar situation for [Ni{ η^2 -(Me₃Si)₂C=PCH-(SiMe₃)₂}(PMe₃)] ($d_{P=C} = 1.773(8)$ Å),³⁸ the first reported η^2 -phosphaalkene complex, which also exhibited an unusually low frequency resonance for the alkenic phosphorus center (δ_P 23). A comparable scenario was recently noted for the only other ruthenium η^2 -phosphaalkene complex, A (Chart 2; $d_{P=C}$

Chart 2. The First (Thus Far Only) η^2 -Phosphaalkene Complex of Ruthenium



= 1.775(3) Å), which provides the sole structural comparison for 5.³⁹ With respect to the phosphaalkene unit, we note contracted Ru–P distances for 5 (2.377(2), 2.308(6) Å) relative to A (2.437(1) Å), while the Ru–C separations lie within the limits of statistical comparability (2.215(6), 2.214(5) Å; cf. A 2.182(3) Å). This can presumably be attributed to the pyrazolyl bridge constraining the proximity of metal and phosphorus centers, whereas A lacks any such constraint.

Interestingly, we first encountered 4 and 5 unexpectedly, as the major products (inter alia intractable trace materials) from the reaction of 3 with KTp' (Tp' = Tp, Tp*), which failed to afford the anticipated pyrazolylborate complexes. Given the absence of detectable levels of free pz'H within the KTp' salts, one must presume fragmentation of the borates, a process that has been documented to complicate the pursuit of "Tp*Ru" complexes.⁴⁰ However, Tp is typically installed without difficulty. Indeed, [TpRu(P=CH^{*}Bu)(CO)(PPh₃)] can be obtained cleanly from 1 and KTp;⁴¹ thus, it would seem reasonable to conclude that the alkenyl substituent (SiMe₃ vs ^tBu) exerts a significant influence upon reactivity, at least in the interaction with azolylborate salts.

Notwithstanding, for the most part, the chemistry of **3** does seemingly mirror that of **1**: in particular, the facility with which it undergoes addition of electrophiles to afford η^1 -phosphaal-kene complexes. Thus, the reaction of **3** with PhHgCl affords [Ru{P(HgPh)=CH(SiMe_3)}Cl_2(CO)(PPh_3)_2] (**6**) exclu-

sively.⁴² The formulation of **6** follows from spectroscopic data,⁴³ in comparison with related systems; thus, the P_{alkenyl} center is significantly shifted (with respect to **3**) to lower frequency ($\delta_{\rm P}$ 406.8) and exhibits satellite coupling to ¹⁹⁹Hg ($J_{\rm HgP}$ = 1792 Hz), alongside a mutual interaction with the retained PPh₃ ligands ($J_{\rm PP}$ = 27 Hz). Proton, carbon, and silicon spectra confirm retention of the other functionalities, while the mercury fragment is apparent from (i) a doublet resonance in the ¹⁹⁹Hg{¹H} spectrum ($\delta_{\rm Hg}$ –845, ¹ $J_{\rm HgP}$ = 1796 Hz) and (ii) the observation of Hg satellites on the ¹³C resonance associated with the phenyl unit. The connectivity was ultimately confirmed by an X-ray diffraction study (Figure 2),⁴⁴ suitable



Figure 2. Molecular geometry of **6** (50% thermal ellipsoids) in crystals of the toluene solvate. The phenyl rings are reduced and hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru1–P1 2.256(2), Ru1–P2 2.399(2), Ru1–P3 = 2.411(2), Ru1–Cl1 = 2.477(2), Ru–Cl2 = 2.469(2), Ru1–C1 = 1.845(5), C1–O1 = 1.139(5), P1–C2 = 1.662(5), P1–Hg1 = 2.390(2), Hg1–C6 = 2.089(5); Ru1–P1–C2 = 126.84(19), Ru1–P1–Hg1 = 117.60(5), Hg1–P1–C2 = 115.37(19), P1–C2–Si1 = 131.4(3).

crystals being obtained by slow cooling of a saturated CH₂Cl₂/ hexane solution. In common with the limited examples of structurally characterized heterodinuclear phosphaalkenyl complexes,^{19b,e} the geometry about Ru is distorted octahedral with interligand angles in the range 84.62(4)–93.43(4)°. The Ru– Cl distances differ beyond 3σ , indicative of a marginally greater *trans* influence for the phosphaalkenyl group (Ru–Cl1 = 2.478(2) Å) vs CO (Ru–Cl2 = 2.469(2) Å); while this is in contrast with the case of [Ru{P(HgFc)=CH^tBu}Cl₂(CO)-(PPh₃)₂] (Fc = ferrocenyl),^{19e} a similar scenario was described for [Ru{P(AuPPh₃)=CH^tBu}Cl₂(CO)(PPh₃)₂].^{19b} The Ru– P1 distance (2.256(2) Å) is markedly shorter than those to the phosphanes (2.411(2), 2.399(2) Å), as was previously observed and attributed to appreciable π acidity of the phosphaalkene ligand.^{19b} Finally of note, the Hg–P(sp²) bond (2.390(2) Å) is somewhat shorter than that reported for the ferrocenyl derivative (2.402(1) Å),^{19e} the only other such linkage known.

In summary, we have reported the unprecedented ambiphilic reactivity of the novel ruthenaphosphaalkenyl complex $[Ru{P=CH(SiMe_3)}Cl(CO)(PPh_3)_2]$ (3) toward nucleophilic *and* electrophilic reagents, *both* leading to functionalization of the phosphorus center. We have thus obtained the first examples of *P*-pyrazolylphosphaalkenes, stabilized within the

metal coordination sphere, viz. $[\operatorname{Ru}\{\eta^{1}-N:\eta^{2}-P,C-P(pz') = CH(\operatorname{SiMe}_{3})\}(CO)(PPh_{3})_{2}]$ (pz' = pz* (4), pz (5)), which represents only the second report of η^{2} -phosphaalkene coordination to ruthenium(0). Addition of electrophilic PhHgCl to 3 affords instead the mercurio-phosphaalkene complex $[\operatorname{Ru}\{P(HgPh) = CH(\operatorname{SiMe}_{3})\}Cl_{2}(CO)(PPh_{3})_{2}]$ (6), only the second such material to be structurally characterized. We have further described the unexpected formation of 4 and 5 via fragmentation of Tp' ligands, in contrast to the facile generation of $[\operatorname{TpRu}(P = CH'\operatorname{Bu})(CO)(PPh_{3})]$, hinting at a significant influence of the alkenyl substituent (SiMe₃ vs 'Bu) upon reactivity, an influence that we continue to explore, alongside the mechanistic features, implications, and wider scope of the nucleophilic derivatization of 3.

ASSOCIATED CONTENT

S Supporting Information

Text, figures, and CIF files giving full experimental details for all compounds, structures of both unique molecules of **5** showing the numbering scheme, and details of the crystal structure determinations of **5** (CCDC 910162) and **6** (CCDC 927274). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(23) Synthesis of 3. To $[RuHCl(CO)(PPh_3)_3]$ (1.00 g, 1.05 mmol) suspended in CH_2Cl_2 was added excess (1.2 equiv) $Me_3SiC \equiv P$ as a solution in toluene. After 2 h, the solvent was removed under reduced pressure and the residue thoroughly agitated with hexane. Anaerobic filtration afforded pure 3, which was dried in vacuo. Yield: 0.8 g, 95%.

(24) Compound 3 was characterized by ³¹P, ¹H, ¹³C{¹H}, ²⁹Si{¹H} NMR and infrared spectroscopy, and elemental analysis. See Supporting Information.

(25) Synthesis of 4 and 5. Typically, to 3 (200 mg, 2.48×10^{-4} mol) suspended in thf (5 cm³) was added 1 equiv of Li(pz') (generated in situ); the mixture was stirred for 1 h at room temperature and the solvent removed at reduced pressure. The residue was extracted into CH₂Cl₂, the extract filtered, and the solvent removed *in vacuo*. Yield: 70%.

(26) Compounds 4 and 5 were characterized by ${}^{31}P$, ${}^{1}H$, ${}^{13}C{}^{1}H$, ${}^{29}Si{}^{1}H$ NMR, infrared spectroscopy and elemental analysis. See Supporting Information.

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(40) See for example: Onishi, M. Bull. Chem. Soc. Jpn. **1991**, 64, 3039. (41) The original report of $[TpRu{P=CH^{t}Bu}(CO)(PPh_{3})]$ describes it as "difficult to obtain in analytical purity" and presents no characterization data.⁴ We have recently obtained this material in purity, confirming the facility of its synthesis: Trathen, N. Unpublished results.

(42) Synthesis of 6. Typically, a solution of 3 (200 mg, 0.248 mmol) in CH_2Cl_2 (10 cm³) was added to a CH_2Cl_2 suspension of 1 equiv PhHgCl. After it was stirred anaerobically for 2 h, the solution was filtered and solvent removed *in vacuo*. Yield = 80%.

(43) Compound **6** was characterized by ${}^{31}P$, ${}^{1}H$, ${}^{13}C{}^{1}H$, ${}^{29}Si{}^{1}H$, ${}^{199}Hg{}^{1}H$ NMR and infrared spectroscopy, and elemental analysis. See Supporting Information.

(44) CCDC 927274. See Supporting Information.