Reactivity of Terminal Electrophilic Phosphinidene Complexes: Synthesis of the First Rhenium Phosphinidene, $[Re(CO)_5(\eta^1\text{-}PN^iPr_2)][AlCl_4]$, and Novel Reactions with Azobenzene

Todd W. Graham, Renan P.-Y. Cariou, Javier Sánchez-Nieves, Anna E. Allen, Konstantin A. Udachin, Rachid Regragui, and Arthur J. Carty*

Steacie Institute for Molecular Sciences, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, Canada K1A 0R6, and The Ottawa-Carleton Chemistry Institute, University of Ottawa, Ottawa, Ontario, Canada K1N 6N5

Received November 19, 2004

Summary: The first terminal rhenium phosphinidene complex, $[Re(CO)_5(\eta^1\text{-}PN^iPr_2)][AlCl_4]$, has been synthesized by chloride abstraction from $[Re(CO)_5\{P(Cl)(N^iPr_2)\}]$. The electrophilic character of the terminal phosphinidene ligand is demonstrated by phosphine addition at the unsaturated phosphorus center and by novel reactions with azobenzene, PhN═NPh, which generate, via C−H activation and P−N and P−C bond formation, coordinated benzodiazaphosphole ligands. The cations $[Re(CO)_5P(PPh_3)N^iPr_2]^+$ and $[Re(CO)_5\{P(PhNNHC_6H_4)N^iPr_2\}]^+$ have been crystallographically characterized as their $AlCl_4^-$ salts. The corresponding late-metal terminal phosphinidene complexes $[Co(CO)_3(PR_3)(\eta^1\text{-}PN^iPr_2)][AlCl_4]$ (R = Ph, Et) also afford coordinated benzodiazaphospholes via reaction with PhN═NPh.

Since the isolation and structural characterization of the first terminal electrophilic phosphinidene complexes in 2001,[1,2] interest in the chemistry of these unsaturated phosphorus analogues of Fischer carbene complexes has expanded considerably.[3−5] Both late-metal compounds, exemplified by (dtbpe)Ni═P(dmp),[3] $[Co(CO)_3(PPh_3)(\eta^1\text{-}PN^iPr_2)][AlCl_4]$,[4] $[(\eta^6\text{-}Ar)LM{=}PMes^*]$ (M = Ru, Os),[5] $[Cp^*M(CO)_2{=}PN^iPr_2]AlCl_4$ (M = Fe, Ru, Os),[6] and $Cp^R(L)M{=}PAr$ (M = Co, Rh, Ir),[7] and complexes of the group 6 metals[1] have been stabilized and isolated. Although their chemistry has not been extensively explored, unlike that of transient species such as $[(OC)_4Fe{=}PR]$[8] and $[(OC)_5W{=}PR]$,[9] there is evidence that the phosphorus center in these compounds is reactive toward unsaturated substrates such as olefins and alkynes, affording cyclic phosphiranes or phosphirenes via phosphinidene group transfer[3] or cycloaddition at the coordinated phosphinidene.[3,4] An extensive chemistry of adducts of these η^1-PR complexes is also developing.[10]

In this communication we describe, inter alia, the synthesis and characterization of the first η^1-phosphinidene complex of rhenium, $[Re(CO)_5(\eta^1\text{-}PN^iPr_2)][AlCl_4]$, and unprecedented reactions of this compound and the related cobalt complex $[Co(CO)_3(PPh_3)(\eta^1\text{-}PN^iPr_2)][AlCl_4]$[4] with the unsaturated nitrogen-containing species azobenzene, PhN═NPh, which afford, via aryl C−H activation and PN_2C_2 ring formation, new coordinated benzodiazaphospholes. These results are in contrast with the only other reported reaction of azobenzene with the transient $[(OC)_5W{=}PR]$ complex, generated in situ, which afforded *o*-phosphino azobenzene derivatives.[11] This suggests that the chemistry of stable η^1-phosphinidenes may differ from that of their transient relatives.[9,11]

The phosphido complex $[Re(CO)_5P(Cl)N^iPr_2]$ (**1**)[12] was readily prepared by the reaction of $Na[Re(CO)_5]$ with $Cl_2PN^iPr_2$. In solution **1**, like its counterpart $[Cp^*Mo(CO)_3(P(Cl)N^iPr_2)]$, is dynamic, with ^{1}H and ^{31}P NMR data[1] indicating restricted rotation about the P−N bond and inversion at the stereogenic phosphorus center. The subsequent addition of $AlCl_3$ to **1** resulted in chloride abstraction and quantitative formation of the Re−phosphinidene species $[Re(CO)_5(\eta^1\text{-}PN^iPr_2)][AlCl_4]$[13] (**2**), as shown in Scheme 1.

* To whom correspondence should be addressed. E-mail: acarty@pco-bcp.gc.ca. Tel: (613) 948-6666. Fax: (613) 948-6667.

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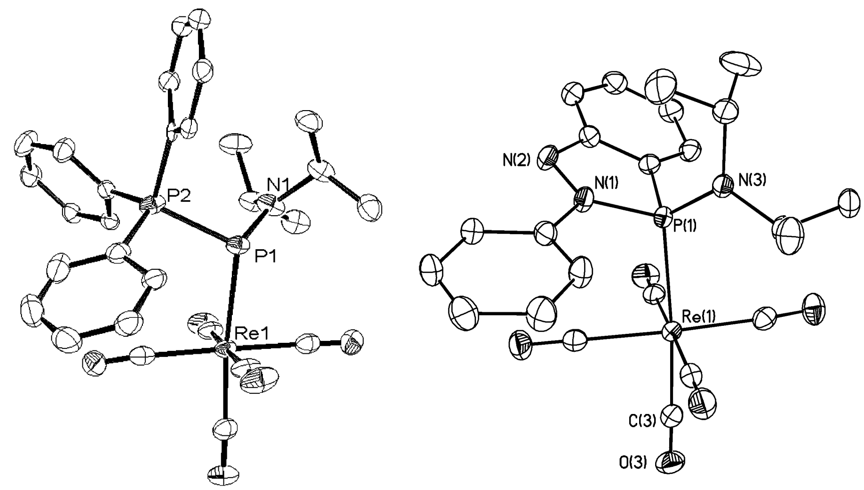
(12) Data for $[Re(CO)_5(P(Cl)N^iPr_2)]$ (**1**) are as follows. Yield: 55%. IR (ν_{CO}, cm^{-1}, hexane solution): 2165 (w), 2060 (w), 2022 (s), 1998 (s). ^{1}H NMR ($CDCl_3$, 25 °C): δ 1.22 (d, 6H, $CH(CH_3)_2$), 1.40 (bs, 6H, $CH(CH_3)_2$), 3.59 (bs, 1H, $CH(CH_3)_2$), 3.90 (bs, 1H, $CH(CH_3)_2$). ^{31}P NMR ($CDCl_3$, 25 °C): δ 214.2. Anal. Calcd for $C_{11}H_{14}O_5PNClRe$: C, 26.82; H, 2.84; N, 2.84. Found: C, 26.83; H, 2.89; N, 2.82.

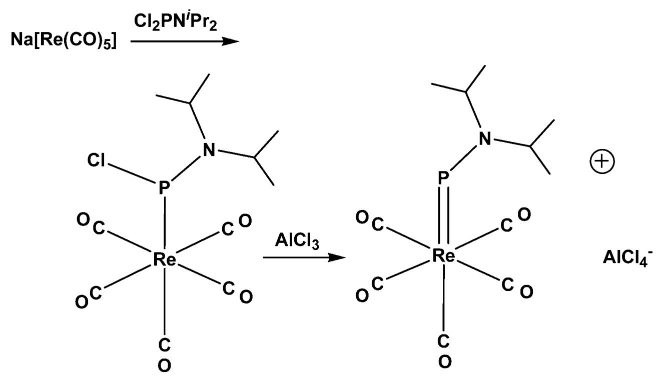
10.1021/om0401307 CCC: $30.25
Publication on Web 03/22/2005



3 **4**

Figure 1. ORTEP diagram of the cations of $[Re(CO)_5(P(N^iPr_2)(PPh_3))][AlCl_4]$ (**3**) and $[Re(CO)_5\{P(PhNNHPh)(N^iPr_2)\}]$-$[AlCl_4]$ (**4**). Hydrogen atoms have been eliminated for clarity, and thermal ellipsoids are shown at the 50% probability level.

Scheme 1



1 **2**

The ^{31}P NMR spectrum of complex **2** has a singlet at δ 956, with a downfield chemical shift characteristic for terminal phosphinidene ligands.[1−7] The ^1H NMR spectrum shows two well-resolved doublets for the ^iPr methyl groups at δ 1.54 and 1.76, with the methine resonances appearing as septets at δ 5.26 and 5.06. The sharpness of these signals indicates severely restricted rotation about the P−N bond, suggesting a significant π interaction between the P and N atoms. A single-crystal X-ray study confirmed the structural identity of **2** as a terminal η^1-phosphinidene complex, and the Re(1)−P(1) (2.446(3) Å) and P(1)−N(1) (1.634(6) Å) bond lengths are comparable to the analogous separations in the related tungsten complex $[Cp^*W(CO)_3(\eta^1\text{-}PN^iPr_2)]$-$[AlCl_4]$ (W(1)−P(1) = 2.4503(6) Å; P(1)−N(1) = 1.629(2) Å).[2] Complex **2** is the first η^1-phosphinidene of the d^7 metals to be reported.

The addition of PPh_3 to complex **2** results in a rapid reaction, affording a species with two ^{31}P NMR resonances appearing as an AB quartet centered at δ 19.4 ($^1J_{PP}$ = 609 Hz).[14] The upfield shift of the Re-bound phosphorus resonance and the large one-bond P−P coupling suggests that nucleophilic addition of the phosphine has occurred at the phosphinidene ligand. This was confirmed by a single-crystal X-ray diffraction experiment, which showed that a species with an unusual P-donor/P-acceptor moiety had formed. The molecular structure of **3** is shown in Figure 1. Compound **3** has a pseudooctahedral ligand arrangement about the rhenium center with five carbonyls and one phosphine ligand bound to the metal. The Re−P(1) separation of 2.5771(7) Å is longer than the Re−P(1) distance in **2** (2.446(3) Å) and corresponds to a single bond;[15] the coordination of PPh_3 to the phosphinidene phosphorus atom P(1) has resulted in a distinctly pyramidalized rhenium-bound phosphorus. The P−P separation of 2.235(1) Å is slightly elongated compared to a typical P−P single bond (e.g. 2.2149(9) Å in $[Cp^*Mo(CO)_2(\eta^2\text{-}P(N^iPr_2)PMe_2CH_2CH_2PMe_2)][AlCl_4]$),[10] and this likely reflects steric interactions between the bulky PPh_3 group and both the N^iPr_2 and $Re(CO)_5$ moieties. Surprisingly, while P(1) is pyramidal and the P−N distance (1.678(2) Å) is significantly longer than in η^1-phosphinidene complexes,[6] N(1) is planar. This may suggest residual π-character in the P−N bond or, more likely, steric resistance to pyramidalization at nitrogen.

Both complex **2** and $[Co(CO)_3(PPh_3)(\eta^1\text{-}PN^iPr_2][AlCl_4]$ readily react with azobenzene. This results in the conversion of the phosphinidene fragment to a coordinated phosphine ligand via nitrogen binding to phosphorus and subsequent C−H activation of an ortho hydrogen, affording the novel benzodiazaphosphole

(13) Data for $[Re(CO)_5(\eta^1\text{-}PN^iPr_2)][AlCl_4]$ (**2**) are as follows. Yield: 94%. IR (ν_{CO}, cm^{-1}, CH_2Cl_2 solution): 2164 (w), 2060 (s), 2014 (w) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ 1.54 (d, 6H, $CH(CH_3)_2$), 1.76 (d, 6H, $CH(CH_3)_2$), 5.26 (sept, 1H, $CH(CH_3)_2$), 5.06 (m, 1H, $CH(CH_3)_2$). ^{31}P NMR ($CDCl_3$, 25 °C): δ 956.1. Anal. Calcd for $C_{11}H_{14}O_5PNCl_4AlRe$: C, 21.15; H, 2.25; N, 2.24. Found: C, 20.63; H, 2.48; N, 1.98.

(14) Data for $[Re(CO)_5\{P(N^iPr_2)(PPh_3)\}][AlCl_4]$ (**3**) are as follows. Yield: 80%. IR (ν_{CO}, cm^{-1}, CH_2Cl_2 solution): 2164 (w), 2140 (w), 2063 (s), 2032 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 0 °C): δ 7.83−7.70 (m, 18H, C_6H_5), 3.34 (s, 2H, CH), 1.05 (s, 6H, $CH(CH_3)_2$), 0.67 (s, 6H, $CH(CH_3)_2$). ^{31}P NMR ($CDCl_3$, 0 °C): δ 20.3 (AB quartet, $^1J_{PP}$ = 609 Hz). Anal. Calcd for $C_{29.5}H_{30}AlCl_5NO_5P_2Re$ (contains 0.5 equiv of cocrystallized CH_2Cl_2): C, 37.42; H, 3.16; N 1.18. Found: C, 36.71; H, 2.92; N, 1.39. Mass spectrum: calcd M^+, *m/z* 720.1; found, *m/z* 720.7. X-ray data: triclinic, $P\bar{1}$, a = 9.7056(5) Å, b = 12.8757(7) Å, c = 15.5502(9) Å, α = 89.1760(10)°, β = 79.1640(10)°, γ = 71.8490(10)°, V = 1811.60(17) Å^3, Z = 2, D_{calcd} = 1.707 Mg/m^3, T = 125(2) K, 9958 independent reflections (R(int) = 0.0275), R1 = 0.0280, wR2 = 0.0666.

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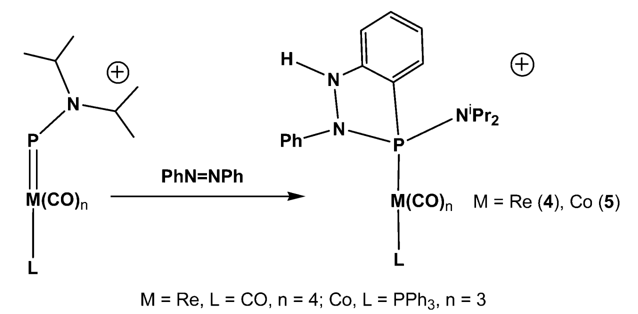
Scheme 2



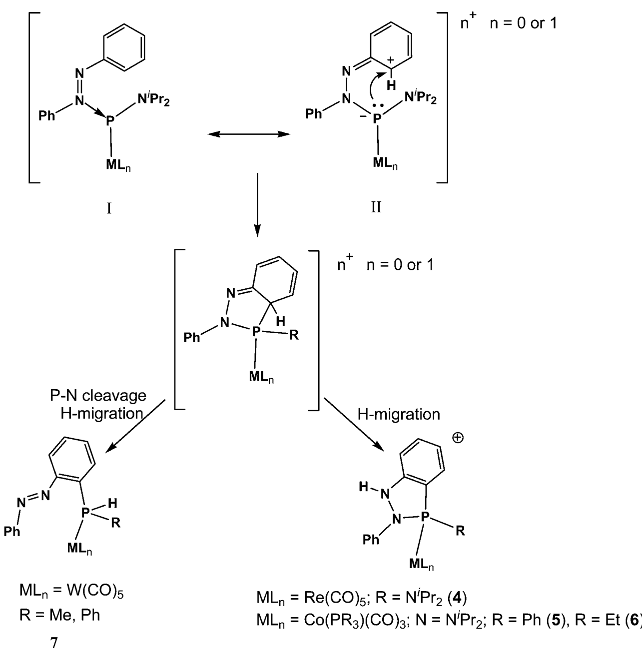
complexes $[Re(CO)_5\{P(PhNNHC_6H_4)(N^iPr_2)\}][AlCl_4]$ (**4**) and $[Co(CO)_3(PPh_3)\{P(PhNNHC_6H_4)(N^iPr_2)\}][AlCl_4]$ (**5**) (Scheme 2).

Complexes **4** and **5** have been characterized via X-ray crystallography.[16,17] The structure of **4**[16] (Figure 1) shows the expected pseudooctahedral ligand environment around the rhenium center and a benzodiazaphosphole ligand that is staggered with respect to the metal-bound carbonyl ligands.

The Re−C(3) distance of 1.986(2) Å is considerably shorter than the M−C bonds of all other carbonyl ligands in the complex (2.005(2), 2.020(2), 2.023(2), and 2.024(2) Å), indicating greater π-back-donation to this CO as a result of the trans tertiary phosphine ligand. As in compound **3**, the phosphorus center is highly pyramidalized and the Re−P bond length of 2.5016(5) Å corresponds to a single bond. The elongated P(1)−N(1) distance (1.712(2) Å) compared to P(1)−N(3) (1.652(2) Å) may be due to strain imposed by the five-membered ring. The geometry about N(3) is planar, as expected from the ^{1}H NMR spectrum[16] of this species, in which the two isopropyl methyl resonances appear as sharp doublets at δ 1.18 and 1.29, apparently a result of severely restricted rotation about the P−N bond. The N−H signal of the coordinated phosphine ligand appears as a broad resonance centered at δ 7.11.

The X-ray structure of compound **5** resembles that of **4**, and so only a few features will be described. The coordination geometry at cobalt is approximately trigonal bipyramidal, with the two phosphine ligands in a trans disposition and the carbonyl groups located in the trigonal plane. The two Co−P bond lengths are very similar (2.2374(4) and 2.2359(4) Å for Co−P(1) and Co−P(2), respectively), a result of the conversion of the phosphinidene fragment in $[Co(PPh_3)(CO)_3(\eta^1\text{-}PN^iPr_2)][AlCl_4]$ to a coordinated benzodiazaphosphole in **5**. The ^{31}P NMR spectrum[17] of this complex shows the expected two doublets at δ 100.3 and 54.3, with the latter signal belonging to the PPh_3 ligand. The 123 Hz coupling is as expected for trans phosphines. The analogous PEt_3 complex $[Co(CO)_3(PEt_3)(P\{PhNNHC_6H_4\}N^iPr_2][AlCl_4]$ (**6**) can be synthesized similarly.[18−20] Complex **6** has a ^{31}P NMR chemical shift identical with that for the benzodiazaphosphole ligand in **5** suggesting the same structure as **5**. To the best of our knowledge, there is no precedent for the synthesis of benzodiazaphosphole ligands as in **4**−**6** from terminal phosphinidenes, and indeed such ligands are rare.

Scheme 3



By analogy with the recently reported reactivity of electrophilic phosphinidenes with phosphines,[10] the initial site of attack by a nitrogen donor atom of azobenzene is likely at the phosphinidene phosphorus. This should result in activation of an ortho carbon to nucleophilic attack due to resonance structure II, shown in Scheme 3. In the final step, proton migration occurs from the six-membered ring to the adjacent azobenzene nitrogen atom.

(16) Data for $[Re(CO)_5\{P(PhNNHC_6H_4)(N^iPr_2)\}][AlCl_4]$ (**4**) are as follows. Yield: 60%. IR (ν_{CO}, cm^{-1}, CH_2Cl_2 solution): 2155 (w), 2093 (w), 2051 (s), 2009 (w) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 25 °C): δ 1.18 (d, 6H, CH(CH_3)$_2$, ^3J(HH) = 6.7 Hz), 1.29 (d, 6H, CH(CH_3)$_2$, ^3J(HH) = 6.6 Hz), 3.81 (m, 2H, CH(CH$_3$)$_2$), 7.11 (s, 1H, NH), 7.42 (m, 9H, Ar). ^{31}P NMR (CD_2Cl_2 25 °C): δ 48.3. Anal. Calcd for $C_{23}H_{24}O_5PN_3Cl_4AlRe$: C, 34.23; H, 2.98; N, 5.21. Found: C, 34.16; H, 3.05; N, 5.18. X-ray data: monoclinic, $P2_1/c$, a = 14.5701(8) Å, b = 14.3060(8) Å, c = 15.6888(9) Å, α = 90°, β = 111.192(1)°, γ = 90°, V = 3049.0(3) Å^3, Z = 4, D_{calcd} = 1.761 Mg/m^3, T = 125(2) K, 7567 independent reflections, R1 = 0.0182, wR2 = 0.0448.

(17) Data for $[Co(CO)_3(PPh_3)\{P(PhNNHC_6H_4)(N^iPr_2)\}][AlCl_4]$ (**5**) are as follows. Yield: 89%. IR (ν_{CO}, cm^{-1}, CH_2Cl_2 solution): 2155 (w), 2093 (w), 2051 (s), 2009 (w) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 25 °C): δ 1.18 (d, 6H, CH(CH_3)$_2$, ^3J(HH) = 6.7 Hz), 1.29 (d, 6H, CH(CH_3)$_2$, ^3J(HH) = 6.6 Hz), 3.81 (m, 2H, CH(CH$_3$)$_2$), 7.11 (s, 1H, NH), 7.42 (m, 9H, Ar). ^{31}P NMR (CD_2Cl_2, 25 °C): δ 48.3. Anal. Calcd for $C_{23}H_{24}O_5PN_3Cl_4AlRe$: C, 34.23; H, 2.98; N, 5.21. Found: C, 34.16; H, 3.05; N, 5.18. X-ray data: monoclinic, $P2_1/c$, a = 16.5189(8) Å, b = 13.5147(6) Å, c = 22.8441(8) Å, α = 90°, β = 122.642(2) °, γ = 90°, V = 4294.4(3) Å^3, Z = 4, D_{calcd} = 1.373 Mg/m^3, T = 125(3) K, 12 025 independent reflections, R1 = 0.0326, wR2 = 0.0808.

(18) Data for $[Co(CO)_3(PEt_3)\{P(Cl)N^iPr_2\}]$ (**6**) are as follows. Yield: 38%. IR (ν_{CO}, cm^{-1}, ether solution): 1972 (s), 1959 (s), 1923 (w). ^{1}H NMR (CD_2Cl_2, −80 °C): δ 1.13 (m, 15H, CH$_2$CH_3 and CH(CH_3)$_2$), 1.24 (d, 3H, CH(CH_3)$_2$, ^3J(HH) = 6.5 Hz), 1.39 (d, 3H, CH(CH_3)$_2$, ^3J(HH) = 6.6 Hz), 1.82 (sept, 6H, CH_2CH$_3$, ^3J(HH) = 7.7 Hz), 3.57 (sept, 1H, CH(CH$_3$)$_2$, ^3J(HH) = 6.5 Hz), 4.42 (sept, 1H, CH(CH$_3$)$_2$, ^3J(HH) = 6.4 Hz). ^{31}P NMR ($CDCl_3$, 25 °C): δ 49.3 (d, PEt$_3$, ^2J(PP) = 17.2 Hz), 284.6 (d, P(Cl)N^{i}Pr$_2$, ^2J(PP) = 18.8 Hz). Anal. Calcd for $C_{15}H_{29}O_3P_2NClCo$: C, 42.12; H, 6.83; N, 3.28. Found: C, 42.14; H, 7.12; N, 3.44.

(19) Data for $[Co(CO)_3(PEt_3)(PN^iPr_2)][AlCl_4]$ (**7**) are as follows. IR (ν_{CO}, cm^{-1}, CH_2Cl_2 solution): 2068 (w), 2015 (s), 1999 (s). ^{1}H NMR ($CDCl_3$, 25 °C): δ 1.25 (m, 9H, CH$_2$CH_3), 1.53 (d, 6H, CH(CH_3)$_2$, ^3J(HH) = 6.0 Hz), 1.63 (d, 6H, CH(CH_3)$_2$, ^3J(HH) = 6.2 Hz), 2.05 (sept, 6H, CH_2CH$_3$, ^3J(HH) = 7.0 Hz), 4.74 (bm, 1H, CH(CH$_3$)$_2$), 5.58 (sept, 1H, CH(CH$_3$)$_2$, ^3J(HH) = 7.0 Hz). ^{31}P NMR ($CDCl_3$, 25 °C): δ 50.2 (s, PEt$_3$), 882.0 (bs, PN^{i}Pr$_2$). Note: this complex decomposes upon attempted isolation.

(20) Data for $[Co(CO)_3(PEt_3)\{P(PhNNHC_6H_4)(N^iPr_2)\}][AlCl_4]$ (**8**) are as follows. Yield: 84%. IR (ν_{CO}, cm^{-1}, CH_2Cl_2 solution): 2068 (w), 2006 (s), 1994 (s). ^{1}H NMR ($CDCl_3$, 25 °C): δ 1.04 (bs, 9H, CH$_2$CH_3), 1.19 (bs, 6H, CH(CH_3)$_2$), 1.40 (bs, 6H, CH(CH_3)$_2$), 1.95 (bs, 6H, CH_2CH$_3$), 4.07 (bs, 2H, CH(CH$_3$)$_2$), 7.50 (bm, 10H, PhNNHPh). ^{31}P NMR ($CDCl_3$, 25 °C): δ 61.0 (d, ^2J(PP) = 107.6 Hz), 100.3 (d, ^2J(PP) = 107.4 Hz). Anal. Calcd for $C_{39}H_{39}O_3P_2N_2AlCl_4Co$: C, 43.63; H, 5.29; N, 5.65. Found: C, 43.10; H, 5.77; N, 6.07.

Mathey and co-workers have reported the reaction of transient [$(OC)_5W{=}PR$] complexes with azobenzene.[11] In this case, however, generation of the phosphinidene in the presence of azobenzene resulted in the formation of an ortho-phosphinated metal complex (**7** in Scheme 3). While the origins of these differences in reactivity between the two metal fragments $W(CO)_5$ and $Re(CO)_5^+$, which are isoelectronic, may relate to higher N−P bond strengths in the cationic intermediates to **4** and **5** (Scheme 3), it is clear that these reactions may lead to synthetically useful and complementary methods for the synthesis of new phosphine ligands. These results add to a growing body of evidence that stable, electrophilic η^1-phosphinidene complexes possess a versatile reaction chemistry driven by nucleophilic and oxidative addition at the highly unsaturated phosphorus center.

Acknowledgment. This work was supported by the National Research Council of Canada and the Natural Sciences and Engineering Research Council of Canada (to A.J.C.).

Supporting Information Available: Text and tables giving synthetic procedures and analytical, spectroscopic, and crystallographic data for compounds **3**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0401307