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Cleavage of Polarized P−P Bonds in N-Heterocyclic Diphosphines in Reactions with Metal Olefin Complexes

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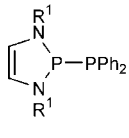
A CC-saturated N-heterocyclic diphosphine was prepared and reacted with $W(CO)_4(cod)$ in acetonitrile to give a mixture of two complexes arising from insertion of an acetonitrile molecule or a metal dicarbonyl fragment, respectively, into the P−P bond of the starting material. Cleavage of P−P bonds was likewise observed upon treating a diphosphine with metal olefin complexes; these reactions proceeded either by metal insertion to give phosphenium−phospholide complexes or via metathesis with formation of a P-chloro N-heterocyclic phosphine (NHP) and transfer of a phospholyl unit to the metal. The newly formed complexes were characterized by spectroscopic data and in several cases by single-crystal X-ray diffraction studies, and mechanistic explanations for the observed product diversity are proposed.

Introduction

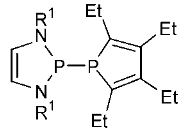
N-heterocyclic diphosphines such as **1a**,**b** (Chart 1) exhibit highly reactive P−P bonds that add under very mild conditions to electron-poor double or triple bonds to give unsymmetrically substituted bidentate 1,2-bisphosphines.[1,2]

As these transformations allow the simultaneous introduction of two P-donor moieties into an organic backbone, they may be regarded as complementary to known approaches to synthesize bidentate O,O or N,N ligands via dihydroxylation[3] or diamination[4] of olefins, respectively. Of special interest is also a recent report on the transition-metal-induced addition of **1b** to a nitrile, which gave directly the chelate complex **2**[2] with a hybrid bidentate P-donor ligand of a type that has recently gathered interest in catalysis;[5] thermolysis of **2** proceeded further via extrusion of the nitrile and produced the complex **3**, which features an intriguing combination of both nucleophilic (phospholide) and electrophilic (phosphenium) ligands and promises a rich, yet unexplored, reactivity (Scheme 1).[2] In order to establish if the facile synthetic approach to **2** and **3** can be used to access a wider range of similar but structurally diverse complexes, it appeared of interest to establish if insertion of a metal atom into a P−P bond is also feasible for diphosphines with P−P bonds less reactive than those in **1a**,**b** or for complexes with metal atoms other than tungsten. We report here on the synthesis of products similar to **2** and **3** from the reaction of a C-saturated N-heterocyclic diphosphine with $(cod)W(CO)_5$ and acetonitrile, the preparation of a phosphenium−phospholide complex of cobalt from Jonas' reagent, $CpCo(C_2H_4)_2$, and a C-unsaturated N-heterocyclic diphosphine, and the reactions of the latter with iron dichloride that occurs likewise with rupture of the P−P bond. A discussion of the results permits us to draw conclusions on some mechanistic aspects of the metal insertion and the scope of this reaction.

Chart 1



1a



1b

Results and Discussion

The C-saturated N-heterocyclic diphosphine **4** was prepared by analogy to the synthesis of **1b**[1] via metathesis of the appropriate cyclic chlorophosphine with tetraethyl lithium phospholide and characterized by spectroscopic and analytical data and a single-crystal X-ray diffraction study. The molecular structure (Figure 1) is characterized by the presence of a twisted rather than planar conformation of the N-heterocyclic ring and a P−P bond (2.346(1) Å) decidedly shorter than in **1b** (2.484(1) Å[1]). The formal CC double and single bonds in the phosphole ring are 1 pm shorter and 2 pm longer, respectively, than in **1b**, and although these differences are on the verge of being significant in relation to the sum of standard deviations, they are in accord with the assumption of a lower degree of P−P bond polarization in **4** that is suggested by the observed change in P−P bond lengths.[1] The ^{31}P NMR data of **4** are distinguished by a noteworthy increase of $^1J_{PP}$ (262 Hz vs 188 Hz for **1b**). The observation of two anisochronic signals for the methylene protons in the N-heterocyclic ring indicates that inversion of the phosphorus atom in the ring is slow on the NMR time scale, whereas the observation of a single set of resonances for the nuclei in the *o*-CH_3 groups of the *N*-mesityl substituents point to unrestricted rotation of the aryl rings around the N−C bonds.

Studies of the interaction of the C-saturated N-heterocyclic diphosphine **4** with $(cod)W(CO)_4$ and acetonitrile revealed that

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[1] Burck, S.; Gudat, D.; Nieger, M. *Angew. Chem.* **2004**, *116*, 4905; *Angew. Chem., Int. Ed.* **2004**, *43*, 4801.

[2] Burck, S.; Gudat, D.; Nieger, M. *Angew. Chem.* **2007**, *119*, 2977; *Angew. Chem., Int. Ed.* **2007**, *46*, 2919.

[3] Kolb, H. C.; VanNieuwenhze, M. S.; Sharpless, K. B. *Chem. Rev.* **1994**, *94*, 2483. Sharpless, K. B. *Angew. Chem.* **2002**, *114*, 2126; *Angew. Chem., Int. Ed.* **2002**, *41*, 2024.

[4] Muniz, K. *New J. Chem.* **2005**, *29*, 1371.

[5] Selected references: Sakai, N.; Mano, S.; Nozaki, K.; Takaya, H. *J. Am. Chem. Soc.* **1993**, *115*, 7033. Nozaki, K.; Sakai, N.; Nanno, T.; Higashijima, T.; Mano, S.; Horiuchi, T.; Takaya, H. *J. Am. Chem. Soc.* **1997**, *119*, 4413. Yan, Y.; Zhang, X. *J. Am. Chem. Soc.* **2006**, *128*, 7198.

10.1021/om801008s CCC: $40.75

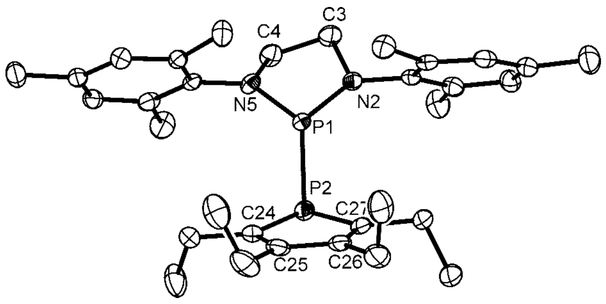
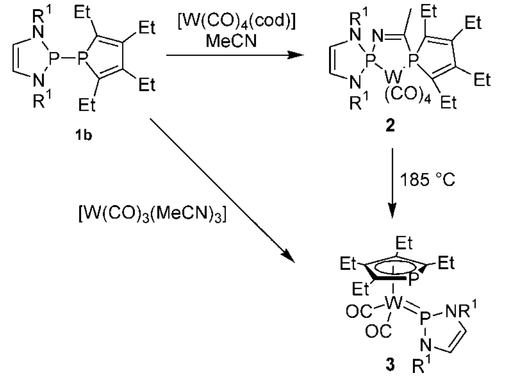


Figure 1. Molecular structure of **4** (H atoms omitted for clarity; 50% probability thermal ellipsoids). Selected bond lengths (Å): P(1)−N(5) = 1.694(1), P(1)−N(2) = 1.710(1), P(1)−P(2) = 2.346(1), N(2)−C(3) = 1.478(2), C(3)−C(4) = 1.509(2), C(4)−N(5) = 1.469(2), N(5)−C(15) = 1.426(2), C(6)−C(11) = 1.403(2), P(2)−C(27) = 1.800(2), P(2)−C(24) = 1.810(2), C(24)−C(25) = 1.365(2), C(25)−C(26) = 1.462(2), C(26)−C(27) = 1.362(2).

Scheme 1[a]



[a] R^1 = 2,4,6-trimethylphenyl.

a reaction was only observed if all three components were present and that the diphosphine **4** reacted, in a fashion similar to that for **1b**,[2] neither with the metal complex nor with acetonitrile alone. However, whereas the formation of **2** from **1b** occurred already at ambient temperature, the reaction of **4** was only observed under more forcing conditions (50 °C) and produced, according to in situ ^{31}P NMR studies, a mixture of the acetonitrile addition product **5** and the nitrile-free phospholyl complex **6** (Scheme 2). Attempts to separate both complexes failed and isolation of pure products on a preparative scale thus remained unfeasible, but **5** was further characterized by an X-ray diffraction study of a single crystal which was serendipitously obtained by manual selection from the isolated product mixture. As in the case of **2**, cleavage of acetonitrile from **5** occurred upon heating to 200 °C and allowed quantitative conversion of the original mixture into **6**, which was isolated by crystallization and unambiguously characterized by analytical and spectroscopic data and a single-crystal X-ray diffraction study.

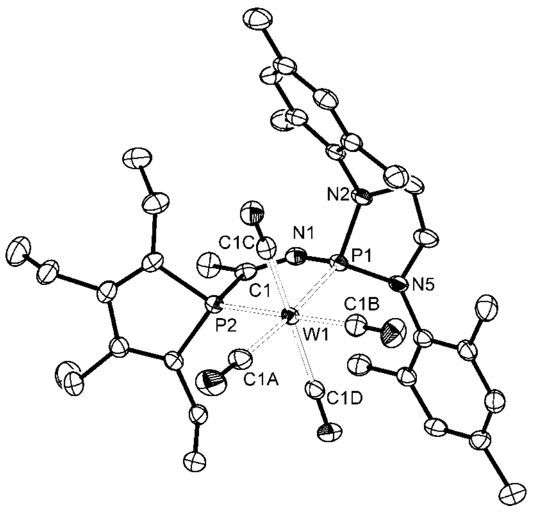
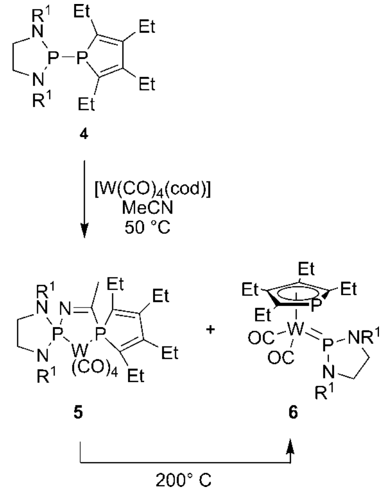


Figure 2. Molecular structure of **5** (H atoms omitted for clarity; 50% probability thermal ellipsoids). Selected bond lengths (Å): W(1)−C(1B) = 1.998(3), W(1)−C(1A) = 2.006(3), W(1)−C(1D) = 2.038(3), W(1)−C(1C) = 2.041(3), W(1)−P(2) = 2.466(1), W(1)−P(1) = 2.476(1), N(1)−C(1) = 1.262(3), N(1)−P(1) = 1.755(2), C(1)−P(2) = 1.882(2), P(1)−N(5) = 1.664(2), P(1)−N(2) = 1.676(2).

Scheme 2[a]



[a] R1 = 2,4,6-trimethylphenyl.

The molecular structures of the complexes **5** and **6** are displayed in Figures 2 and 3, respectively. The X-ray diffraction study confirms the coordination of a cis-substituted tungsten tetracarbonyl fragment by a chelating bis-phosphine for **5** and a piano-stool like geometry with a η^5-bound phospholyl moiety for **6**. The terminal phosphenium ligand in **5** displays a planar coordination of the phosphorus atom. The N-heterocyclic rings in **5** and **6** are not planar as in **2** and **3** but adopt a flat twist conformation. Although the individual bond distances in **5** and **6** differ numerically from the corresponding values for **2** and **3**,[2] respectively, these deviations are (apart from the deviation in N−C and C−C bonds involving sp^2 and sp^3 carbon atoms in the N-heterocycles) not significant in relation to the estimated standard deviations and will not be discussed further. The spectroscopic data of **5** and **6** likewise closely resemble those of the species **2** and **3** with C-unsaturated N,P-heterocycles. The change from a formal bis-phosphine (**5**) to a phosphenium−phospholide (**6**) coordination mode environment is reflected by a strong increase of both $\delta(^{31}P)$ and $^1J_{WP}$ for the phosphorus atom in the phosphenium moiety, which is indicative of partial M−P double-bond character;[6] at the same time, the switch from η^1 to η^5 coordination of the phospholyl moiety induces a strong shielding of the phosphorus resonance and a decrease of $^1J_{WP}$ to a value of 0.

If one considers that **5** is stable in solution up to temperatures of at least 100 °C and that its conversion into **6** occurs only around 200 °C, it appears unreasonable to postulate **5** as an intermediate in the formation of **6** during the reaction of **4** and

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(6) Cowley, A. H.; Kemp, R. A. *Chem. Rev.* **1985**, *85*, 372. and literature cited therein.

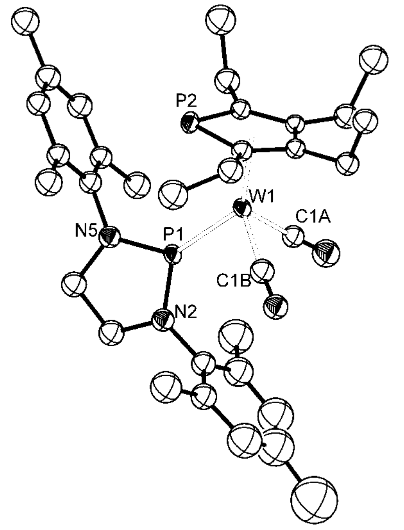
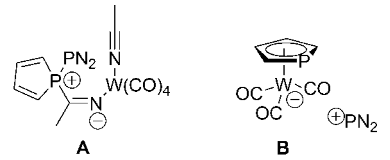


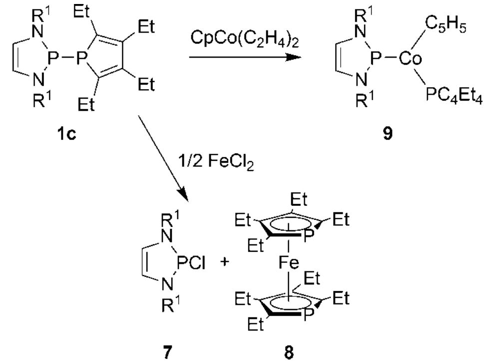
Figure 3. Molecular structure of one of the two crystallographically independent molecules of **6** (H atoms omitted for clarity; 50% probability thermal ellipsoids; only W and P atoms refined anisotropically). Selected bond lengths (Å) (values in brackets denote bond lengths for the second molecule): W(1)−C(1B) = 1.933(15) [1.922(15)], W(1)−C(1A) = 1.937(14) [1.959(17)], W(1)−P(1) = 2.223(3) [2.223(4)], W(1)−P(2) = 2.572(4) [2.566(4)], W(1)−cent = 2.021(6) [1.959(6)], P(1)−N(2) = 1.647(12), [1.665(12)], P(1)−N(5) = 1.666(12) [1.643(12)].

Chart 2



W(CO)$_4$(cod). We propose therefore an alternative mechanism which explains the formation of both products via a common precursor and allows us at the same time to rationalize the previously reported behavior of **1**.[2] Following this model, we suggest that the reaction is initiated by displacement of cyclooctadiene by two nitrile ligands and subsequent attack of a coordinated CN triple bond by the nucleophilic phospholyl moiety of the diphosphine. A plausible structure of a resulting key intermediate is formulated as **A** (Chart 2), which resembles the betaines arising from interaction of electron-deficient alkynes with tertiary phosphines[7] or diphosphines.[8] Since we had previously established that interaction of the phosphinyl moiety in **1** with electrophiles facilitates P−P bond dissociation,[9] it is reasonable to assume that the next reaction step involves heterolytic P−P bond fission. The observed products **2** and **5** are finally formed via migration of the phosphenium cation fragment to the imino nitrogen atom, extrusion of the remaining nitrile ligand, and coordination of both phosphine donor moieties to the metal atom.[10] Since the increased P−P bond lengthening in **1b** as compared to the bonds in **4** must be considered to facilitate the bond-breaking step,[1,9] the different reaction temperatures in both cases are easily rationalized. The fact that a phosphenium−phospholide complex (**6**) is formed in the reaction with **4**, but not with **1b**, is rationalized by postulating that the nitrile-containing intermediates (**A** or its successors) are thermally labile and may easily lose both nitriles at elevated temperature. Stabilization of the coordinatively unsaturated metal atom may then occur by a switch from η^1(P) to π coordination of the phospholyl ligand, and it is conceivable that after additional loss of one carbonyl the transient π-phospholyl complexes **B** are produced. Conversion of these intermediates into the final products **3** and **6** via recombination of the ionic fragments and decarbonylation is a known reaction that has precedence in the formation of a previously described phosphenium−cobalt complex.[11] The mechanistic hypothesis is further supported by the observation that reaction of **1b** with W(CO)$_3$(MeCN)$_3$ yields likewise a mixture of the nitrile addition product **2** and the phosphenium−phospholide complex **3** unless performed under strict temperature control (formation of **3** is obviously facilitated by a lower number of stabilizing carbonyl ligands and thus an increased thermal lability for W(CO)$_3$(MeCN)$_3$ as compared to W(CO)$_4$(MeCN)$_2$).[12] Although insertion into the P−P bond of symmetrical diphosphines has been shown to follow a radical mechanism,[13] we want to rule out this alternative in the present case, as **1b** (which reacts with (cod)W(CO)$_4$/nitrile to give the same products as **4**) had definitely previously been disproved to undergo similar radical reactions,[1] and even the reactions of alkynes with diphosphines having P−P bonds less polar than in **4** have been considered to proceed via heterolytic rather than homolytic bond cleavage.[8]

Scheme 3[a]



[a] R^1 = 2,6-Me$_2$C$_6$H$_4$.

In order to establish the feasibility of P−P bond activation with metals other than tungsten, we studied the behavior of the more reactive diphosphine **1c**[1] toward anhydrous iron dichloride and CpCo(C$_2$H$_4$)$_2$ (Jonas' reagent), respectively. Analysis of ^{31}P NMR spectra of reaction solutions of **1c** and FeCl$_2$ indicated formation of a 1:1 mixture of the chlorophosphine **7**[14] and the diphosphaferrocene **8**[15] (Scheme 3). Separation of the products by selective extraction with hexane proved unfeasible, and further attempts toward isolation of pure compounds were thus

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(8) Dodds, D. L.; Haddow, M. F.; Orpen, A. G.; Pringle, P. G.; Woodward, G. *Organometallics* **2006**, *25*, 5937.

(9) Gudat, D.; Burck, S.; Nieger, M.; Vinduš, D. *Eur. J. Inorg. Chem.* **2008**, 704.

(10) The exact sequence of the individual steps and the nature of any further intermediates formed must currently remain undecided.

(11) Burck, S.; Daniels, J.; Gans-Eichler, T.; Gudat, D.; Nättinen, K.; Nieger, M. *Z. Anorg. Allg. Chem.* **2005**, *631*, 1403.

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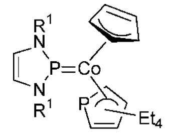
(13) Bezombes, J. P.; Hitchcock, P. B.; Lappert, M. F.; Nycz, J. E. *Dalton Trans.* **2004**, 499.

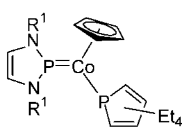
(14) Burck, S.; Gudat, D.; Nättinen, K.; Nieger, M.; Niemeyer, M.; Schmid, D. *Eur. J. Inorg. Chem.* **2007**, 5112.

(15) Sava, X.; Ricard, L.; Mathey, F.; Le Floch, P. *Organometallics* **2000**, *19*, 4899.

Chart 3



10'

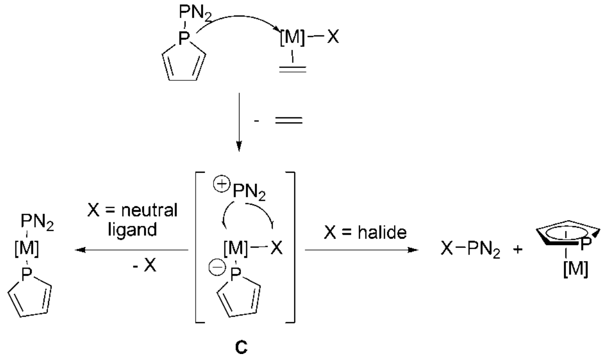


10''

abandoned, but both products were unambiguously identified by comparison of their spectroscopic data with those of authentic samples.[16]

Reaction of **1c** with $CpCo(C_2H_4)_2$ proceeded with gas evolution (C_2H_4) to produce a dark-colored solution from which a black crystalline product was isolated. The crystals were unsuitable for a single-crystal X-ray diffraction study, but analytical and spectroscopic (NMR, MS) data allowed unambiguous identification of the product as cobalt complex **10**. The presence of a phospholyl, a cyclopentadienyl, and a N-heterocyclic phosphenium moiety is clearly evident from the ^{1}H and ^{13}C NMR spectra, and the observation of two ^{31}P NMR signals connected by a homonuclear coupling (32 Hz) proves that both phosphorus-containing ligands are attached to the metal but are no longer directly bonded. The substantial broadening of the signal of the N-substituted phosphorus atom by partially collapsed scalar coupling to the quadrupolar ($I = {}^7/_2$) ^{59}Co nucleus indicates that the coupling constant $^1J_{CoP}$—although not directly measurable—is of substantial magnitude and is a typical characteristic of phosphenium complexes with a formal M—P double bond and planar coordination at phosphorus.[11] In contrast, the narrow line width of the other signal reveals that $^1J_{CoP}$ is small and suggests that coordination of the phospholyl ligand occurs via the π system or in an η^1 mode which does not involve the phosphorus lone pair.[17] The C_5H_5 moiety gives rise to a single ^{1}H and ^{13}C NMR signal, respectively, which display the typical chemical shifts of a π-coordinated ligand. If one assumes for the metal atom in **10** a valence electron (VE) count of 18 and considers that a phosphenium—Co(I) fragment contributes 10 VE, the molecular structure can be described by either of the two models shown in Chart 3. In the first case, the Cp^- and phospholide ligands represent η^3-bound 4-VE donors and must be fluxional to match the observed NMR data, whereas the second structure contains η^5-Cp and η^1-phospholyl moieties;[18] both η^1 [17,19] and η^3 binding modes[20] of phospholyl ligands have precedents in the literature. An alternative assumption that **10** features both rings in an η^5 binding mode as in phosphacobaltocenes[21] and phosphanickelocenes[19] with formal 19- and 20-VE counts is unlikely, as it appears unreasonable to assume that an anionic 20-VE $[CpCo(phospholyl)]^-$ moiety should coordinate a further cationic diazaphospholenium moiety to give a complex with a formal valence electron count of 22. Even though **10''** seems to be better in accord with the observed chemical shifts, a reliable distinction between both models is unfeasible from the available spectroscopic data.

Scheme 4. Schematic Representation of the Proposed Reaction Mechanism for the Reaction of N-Heterocyclic Diphosphines with Metal Olefin Complexes



If one assumes that the previously described reactions are likewise initiated by displacement of a coordinated alkene unit by the phosphole moiety of **1c** to give a betaine-like structure similar to **A**, their course can be rationalized by a similar mechanism involving subsequent P—P bond cleavage to give the putative intermediate **C** (Scheme 4) and, finally, electrophilic attack of the phosphenium cation at the counteranion to produce the observed products. Whereas in the reaction with Jonas' reagent the metal atom remains the only nucleophilic center, intermediates derived from metal chlorides possess two nucleophilic sites in the metal and the chlorine atom. The observed regioselectivity—attack at the chlorine atom to give metathesis products rather than interaction with the metal atom—is in accord with the previous finding[22] that N-heterocyclic phosphenium atoms seem to prefer charge-controlled reactions with harder Lewis bases over orbital-controlled reactions with softer bases.

Conclusions

Comparison of the reactivity of the N-heterocyclic diphosphines **1b** and **4** toward acetonitrile/$W(CO)_4$(cod) indicates that the P—P bond strength in the starting material influences the competition between a reaction under direct oxidative addition of the P—P bond to the metal atom and the diphosphination of the nitrile triple bond, respectively, and that high P—P bond reactivity in the diphosphine is crucial for the observation of the unusual nitrile activation. The reactivity of **1c** toward further low-valent metal olefin complexes reveals that P—P cleavage reactions indeed have a larger scope and proceed either via metathesis under transfer of only a phospholyl unit to the metal or via insertion under transfer of both a phospholyl and a phosphenium unit. The available results suggest that the selection between both pathways depends on the ability of the metal complex to act as ambident nucleophile, with metal halides featuring a hard Lewis base center preferring the metathesis reaction.

Experimental Section

All manipulations were carried out under an atmosphere of dry argon using standard vacuum line techniques. Solvents were dried

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(16) Similarly, reaction of **1c** with $[(cod)RhCl]_2$ gave, according to a ^{31}P NMR survey, a mixture of **7** and a complex assigned as (tetraethylphospholyl)(cyclooctadiene)rhodium(I) on the basis of the similarity of the observed NMR data ($\delta(^{31}P)-4.1$, $^1J_{RhP} = 3.8$ Hz) to those of the known complex (2,5-di-*tert*-butylphospholyl)(cyclooctadiene)rhodium(I) ($\delta(^{31}P)-3.8$, $^1J_{RhP} = 15.2$ Hz); see: Forissier, K.; Ricard, L.; Carmichael, D.; Mathey, F. *Chem. Commun.* **1999**, 1273.

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(18) A third alternative comprising a fluxional η^1-Cp and a η^5-phospholyl ligand appears unlikely, in view of the observed $\delta(^{13}C)$ values of the carbon atoms in both rings.

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(22) Burck, S.; Gudat, D. *Inorg. Chem.* **2008**, *47*, 315.

Table 1. Crystallographic Data and Summary of Data Collection and Refinement for 4−6

	4	**5**	**6**
formula	$C_{32}H_{46}N_2P_2$	$C_{38}H_{49}N_3O_4P_2W$	$C_{34}H_{46}N_2O_2P_2W$
formula wt	520.65	857.59	760.52
cryst size, mm	0.40 × 0.30 × 0.20	0.30 × 0.20 × 0.20	0.45 × 0.20 × 0.10
cryst syst; space group	monoclinic; $P2_1/n$	orthorhombic; *Pbca*	monoclinic; *C*2/*c*
unit cell dimens			
a, Å	9.7825(2)	14.5680(1)	23.8525(5)
b, Å	22.4622(4)	20.7786(1)	18.1101(4)
c, Å	13.7718(3)	25.2384(2)	34.0334(6)
β, deg	90.014(2)		98.180(1)
V, Å^3	3026.17(11)	7639.73(9)	14551.9(5)
Z; ρ_{calcd}, Mg/m^3	4; 1.14	8; 1.49	16; 1.39
μ, mm^{-1}	0.166	3.149	3.292
$F(000)$	1128	3472	6144
θ range for data collecn, deg	3.0−27.5	3.0−27.5	2.9−25.0
completeness of data for $\theta = 25°$, %	99.8	99.7	96.7
limiting indices	$-12 \le h \le 7$, $-29 \le k \le 22$, $-17 \le l \le 17$	$-18 \le h \le 18$, $-26 \le k \le 25$, $-32 \le l \le 32$	$-28 \le h \le 23$, $-20 \le k \le 21$, $-27 \le l \le 40$
no. of collected/unique rflns	21 121/6837 ($R_{int} = 0.044$)	67 805/8682 ($R_{int} = 0.054$)	29 175/12 438 ($R_{int} = 0.101$)
abs cor	none	semiempirical from equivalents.	semiempirical from equivalents
max, min transmissn		0.535 73, 0.466 49	0.463 80, 0.304 45
no. of data/restraints/params	6837/0/331	8682/0/440	12 438/0/371
goodness of fit on F^2	1.026	1.038	1.015
R1 ($I > 2\sigma(I)$)	0.040	0.024	0.080
wR2 (all data)	0.107	0.060	0.217
largest diff peak, hole, e Å^{-3}	0.354, −0.282	1.996, −1.600	4.579, −1.758

by standard procedures. NMR spectra were recorded on Bruker Avance 400 (^{1}H, 400.1 MHz; ^{13}C, 100.5 MHz; ^{31}P, 161.9 MHz) and Avance 250 (^{1}H, 250.1 MHz; ^{13}C, 62.8 MHz; ^{31}P, 101.2 MHz) NMR spectrometers at 303 K; chemical shifts are referenced to external TMS (^{1}H, ^{13}C) or 85% H_3PO_4 ($\Xi = 40.480\,747$ MHz, ^{31}P). Coupling constants are given as absolute values; i, o, m, and p denote the positions in phenyl and 2,6-dimethylphenyl (DMP, denoted as C_6H_3) rings. EI-MS was carried out on a Varian MAT 711 instrument at 70 eV. Elemental analyses were determined on a Perkin-Elmer 24000CHN/O analyzer. Melting points were determined in sealed capillaries.

1,3-Dimesityl-2-(2′,3′,4′,5′-tetraethylphospholyl)tetrahydro-1,3,2-diazaphosphole (4). Lithium (70 mg, 10 mmol) was added to a solution of 1-chloro-2,3,4,5-tetraethylphosphole (1.15 g, 5 mmol) in THF (50 mL) and the mixture stirred for 3 h at room temperature. Unreacted metal was filtered off, and the solution was added dropwise to a cooled (−78 °C) solution of 1-chloro-1,3-dimesityltetrahydro-1,3,2-diazaphosphole (1.81 g, 5 mmol) in THF (100 mL). After the addition was finished, the mixture was warmed to room temperature and stirred for 1 h more. Volatiles were evaporated under vacuum, the residue was dissolved in hexane (100 mL), and this solution was filtered over Celite. The filtrate was concentrated under reduced pressure to a total volume of 30 mL and stored at −20 °C for crystallization. Yellow crystals separated that were collected by filtration and dried under vacuum: yield 1.87 g (69%); mp 101 °C. ^{1}H NMR (C_6D_6): δ 6.75 (s, 4 H, m-CH), 3.53 (m, 2 H, N−CH_2), 2.82 (m, 2 H, N−CH_2), 2.40 (s, 12 H, o-CH_3), 2.20 (q, $^3J_{HH} = 7.3$ Hz, 4 H, CH_2), 2.10 (s, 6 H, p-CH_3), 2.01 (m, 2 H, CH_2), 1.9 (m, 2 H, CH_2), 1.07 (t, $^3J_{HH} = 7.5$ Hz, 6 H, CH_3), 0.90 (t, $^3J_{HH} = 7.3$ Hz, 6 H, CH_3). ^{13}C{^{1}H} NMR (C_6D_6): δ 151.6 (d, $^2J_{PC} = 5.2$ Hz, i-C), 142.9 (dd, $^1J_{PC} = 17.6$ Hz, $^2J_{PC} = 11.4$ Hz, C(phosphole)), 139.9 (dd, $J_{PC} = 12.7$, 1.1 Hz, C(phosphole)), 136.2 (broad s, o-C), 134.9 (dd, $^4J_{PC} = 1.9$ Hz, $^5J_{PC} = 0.1$ Hz, m-C), 130.3 (d, $^5J_{PC} = 1.1$ Hz, p-C), 54.0 (dd, $J_{PC} = 7.9$, 0.3 Hz, N−CH_2), 21.7 (dd, $J_{PC} = 20.7$, 1.6 Hz, CH_2), 21.3 (dd, $^4J_{PC} = 1.5$ Hz, $^5J_{PC} = 0.6$ Hz, o-CH_3), 20.8 (d, $^6J_{PC} = 0.6$ Hz, m-CH_3), 20.6 (dd, $^3J_{PC} = 8.3$ Hz, $^4J_{PC} = 2.3$ Hz, CH_2), 18.6 (dd, $^3J_{PC} = 5.4$ Hz, $^4J_{PC} = 1.7$ Hz, CH_3), 16.2 (d, $^4J_{PC} = 1.3$ Hz, CH_3). ^{31}P{^{1}H} NMR: δ 143.1 (d, $^1J_{PP} = 261.6$ Hz, N_2P), 9.1 (d, $^1J_{PP} = 261{,}6$ Hz, P(phosphole)). MS (EI, 70 eV, 400 K): *m/e* (%) 520.3 (0.3) [M]$^+$, 325.2 (100) [M − $C_{12}H_{20}P$]$^+$, 196.1 (42) [M − $C_{20}H_{25}N_2P$]$^+$, 148.1 (54). Anal. Calcd for $C_{32}H_{46}N_2P_2$ (520.68): C, 73.82; H, 8.91; N, 5.38. Found: C, 73.43; H, 8.96; N, 5.32.

Reaction of 4 with (cod)W(CO)$_4$. A solution of (cod)W(CO)$_4$ (810 mg, 2 mmol) in CH_3CN (30 mL) was added dropwise to a solution of **4** (1.36 g, 2 mmol) in CH_3CN (30 mL), and the resulting mixture was stirred for 4 h at 50 °C. Formation of a mixture of **5** and **6** was established by ^{31}P NMR. Attempts toward separation of the reaction products by evaporation of volatiles and fractionating crystallization from hexane failed and produced a precipitate consisting of a mixture of crystals of both specimens. Manual separation of the different sorts of crystals on a large scale was unfeasible, but **5** could be further characterized by a single-crystal X-ray diffraction study of a manually selected single crystal. ^{31}P{^{1}H} NMR (C_6D_6): δ 218.1 (d, $^2J_{PP} = 10.2$ Hz, $^1J_{PW} = 718$ Hz, N_2P, **6**), 158.2 (d, $^3J_{PP} = 28.8$ Hz, $^1J_{PW} = 154$ Hz, **5**), 100.1 (d, $^3J_{PP} = 28.8$ Hz, $^1J_{PW} = 119$ Hz, **5**), −16.1 (d, $^2J_{PP} = 10.2$ Hz, **6**). IR (KBr, Nujol): 2017 (**5**), 1920 (**6**), 1905 (**5**), 1881 (**6**), 1856 cm^{-1} (**5**).

Dicarbonyl-2-(1,3-dimesityltetrahydro-1,3,2-diazaphospholyl)(η^5-2′,3′,4′,5′-tetraethylphospholyl)tungsten(0) (6). The crude mixture of **5** and **6** (1.72 g) was placed in a Schlenk tube and heated briefly to 200 °C. The dark-colored melt was allowed to cool to ambient temperature and dissolved in toluene (10 mL). Storage of the solution at −20 °C produced a yellow crystalline precipitate, which was collected by filtration and dried under vacuum: yield 1.40 g (92%); mp 199 °C. ^{1}H NMR (C_6D_6): δ 6.93 (s, 4 H, m-CH), 3.77 (d, $^3J_{PH} = 4.5$ Hz, 4 H, N−CH_2), 2.52 (m, 4 H, CH_2), 2.37 (s, 12 H, o-CH_3), 2.29 (s, 6 H, p-CH_3), 2.29 (m, 4 H, CH_2), 2.10 (dq, $^2J_{HH} = 7.4$ Hz, $^3J_{HH} = 7.4$ Hz, 2 H, CH_2), 1.68 (dq, $^2J_{HH} = 7.6$ Hz, $^3J_{HH} = 7.6$ Hz, 2 H, CH_2), 1.05 (t, $^3J_{HH} = 7.6$ Hz, 6 H, CH_3), 0.79 (t, $^3J_{HH} = 7.4$ Hz, 6 H, CH_3). ^{31}P{^{1}H} NMR (C_6D_6): δ 220.1 (d, $^1J_{PW} = 718$ Hz, $^2J_{PP} = 10.3$ Hz, N_2P), −16.0 (d, $^2J_{PP} = 10.3$ Hz, P(phosphole)). IR (KBr, Nujol): 1920, 1881 cm^{-1}. MS (EI, 70 eV, 430 K): *m/e* (%) 760.3 (100) [M]$^+$, 732.0 (6) [M − CO]$^+$, 704.0 (14) [M − 2CO]$^+$, 325.2 (81) [$C_{20}H_{26}N_2P$]$^+$. Anal. Calcd for $C_{34}H_{46}N_2O_2P_2W$ (760.55): C, 53.69; H, 6.20; N, 3.68. Found: C, 54.41; H, 6.46; N, 3.46.

Reaction of 1c with FeCl$_2$. 1c (49 mg, 0.1 mmol) and anhydrous $FeCl_2$ (10 mg, 0.05 mmol) were dissolved in C_6D_6. Quantitative conversion of the starting materials into the products was established by ^{31}P and ^{1}H NMR spectroscopy. The products were identified by comparison of the data with those of authentic samples; no attempts toward separation or isolation were made. ^{1}H NMR (C_6D_6): δ 6.96 (broad, 6 H, m-/p-CH), 5.78 (broad, 2 H, N−CH), 2.45 (broad, 4 H, CH_2), 2.35 (broad, 4 H, CH_2), 2.19 (s, 12 H, o-CH_3), 1.20 (broad, 6 H, CH_3), 1.09 (broad, 6 H, CH_3). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 147.8 (s, **7**), −62.9 (broad s, **8**).

(η^1-Cyclopentadienyl)(η^1-1,3-bis(2′,6′-dimethylphenyl)-2,3-dihydro-1,3,2-diazaphospholyl)(η^5-2,3,4,5-tetraethylphospholyl)cobalt(I) (9). A solution of **1** (343 mg, 0.7 mmol) and $CpCo(C_2H_2)_2$ (126 mg, 0.7 mmol) in dry THF (10 mL) was stirred for 1 h. Volatiles were then removed under reduced pressure, the residue was dissolved in pentane (10 mL), and this solution was stored at −20 °C. Black crystals formed, which were collected by filtration and dried under vacuum: yield 342 mg (81%); mp 155 °C. ^1H NMR (C_6D_6): δ 6.85−7.00 (m, 6 H, m-/p-H), 5.64 (d, $^3J_{PH} = 6.7$ Hz, 2 H, N−CH), 3.90 (s, 5 H, Cp), 2.32−2.78 (m, 8 H, CH_2), 2.33 (s, 12 H, o-CH_3), 1.27 (t, $^3J_{HH} = 7.5$ Hz, 6 H, CH_3), 1.22 (t, $^3J_{HH} = 7.5$ Hz, 6 H, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 142.9 (d, $^1J_{PC} = 6.1$ Hz, PC(phosphole)), 139.4 (d, $^2J_{PC} = 5.7$ Hz, i-C), 136.3 (s, o-C), 128.9 (s, p-CH), 128.8 (s, m-CH), 122.4 (dd, $^2J_{PC} = 2.3$ Hz, $^4J_{PC} = 1.0$ Hz, N-CH), 82.3 (d, $^2J_{PC} = 2.9$ Hz, Cp), 23.2 (d, $^2J_{PC} = 21.8$ Hz, CH_2), 22.3 (s, CH_2), 18.7 (d, $^3J_{PC} = 7.4$ Hz, CH_3), 18.6 (s, o-CH_3), 16.8 (d, $^3J_{PC} = 4.0$ Hz, CH_3). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 157.5 (broad, N_2P), −81.0 (d, $^2J_{PP} = 32.4$ Hz, PC_4). MS (EI, 70 eV, 410 K): *m/e* (%) 614.3 (<0.1) [M]$^+$, 419.1 (<0.1) [M − Et_4-phospholyl]$^+$, 319.1 (100) [CpCo(Et_4-phospholyl)]$^+$, 295.0 (37) [$C_{18}H_{20}PN_2$]$^+$. Anal. Calcd for $C_{35}H_{45}N_2P_2Co$ (614.64): C, 68.40; H, 7.38; N, 4.56. Found: C, 67.93; H, 7.36; N, 4.12.

Crystallography. The crystal structure determinations of **4**−**6** were performed on a Nonius KappaCCD diffractometer at 123(2) K using Mo Kα radiation ($\lambda = 0.710\,73$ Å). Crystal data, data collection parameters, and results of the analyses are given in Table 1. Direct methods (SHELXS-97)[23] were used for structure solution, and refinement was carried out using SHELXL-97 (full-matrix least squares on F^2).[23] Hydrogen atoms were refined using a riding model. Due to the low quality of the diffraction data of **6**, only the W and P atoms were refined anisotropically. There are large voids (approximately 400 Å^3) in the structure. These voids probably contain highly disordered solvent (toluene), which could not be refined reasonably. Application of SQUEEZE suggested that these voids should contain approximately 800 electrons, or 16 molecules of toluene, but this did not help to improve the quality of the structure.

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Supporting Information Available: CIF files giving X-ray structural information on **4**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org. In addition CCDC-704594 (**4**), CCDC-704595 (**5**), and CCDC-704596 (**6**) contain supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[23] Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112.