Electrophilic Reactions of Zerovalent Tungsten Nitrene and Hydrazido Complexes with Phosphines. Synthesis and Structure of $(CO)_4\overline{W[PPh_2CH_2PPh_2N}NMe_2]$

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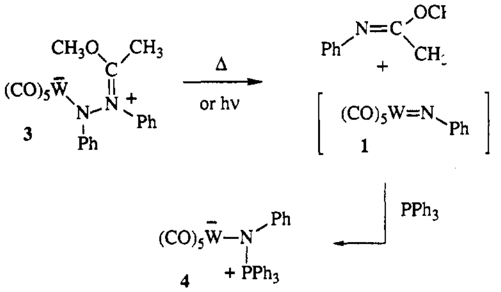
The low-valent hydrazido complex $(CO)_5W{=}NNMe_2$ (**2**) reacts with bis(diphenylphosphino)methane (DPPM) to yield the metallacyclic phosphinimine complex $(CO)_4\overline{W[PPh_2CH_2PPh_2N}NMe_2]$ (**5**). Mechanistic studies and extended Hückel molecular orbital calculations suggest that formation of **5** occurs via a highly unusual nucleophilic attack of phosphine at N_α of the hydrazido ligand. Complex **5** has been characterized spectroscopically as well as by X-ray crystallography: $P2_1/n$; $a = 10.797(3)$ Å, $b = 22.761(3)$ Å, $c = 12.257(2)$ Å, $\beta = 90.92(4)°$, $V = 3011.8(11)$ Å^3, $Z = 4$, $R(F) = 3.87\%$, $R(wF) = 4.69\%$, for 4292 reflections, $F \geq 5.0\sigma(F)$.

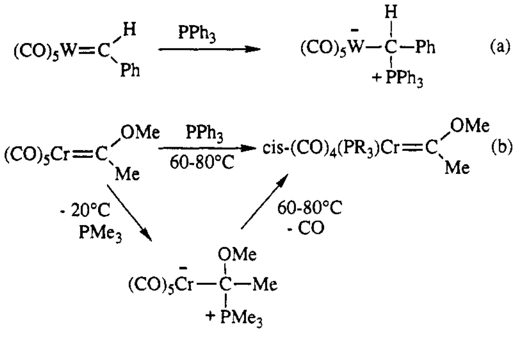
Introduction

Several examples of zerovalent nitrene (or imido) complexes of the general form $L_5M{=}NR$ (M = Cr, Mo, W; L = phosphine, carbonyl; R = aryl, dialkylamino) have been recently reported.[1] These compounds show certain structural[1d] and reactivity[1a–d] characteristics that parallel those of the Fischer carbenes, species that have been of great synthetic interest due to their ability to transfer the carbene moiety to organic molecules.[2] One intriguing property of these metal–nitrenes is the observed electrophilicity of the nitrogen, demonstrated by the reaction of $(CO)_5W{=}NPh$ (**1**) with PPh_3 (Scheme I).[1a] Such electrophilic reactivity is very common for the carbene carbon of Fischer carbenes, as is illustrated in their reactions with phosphines to generate ylide complexes (Scheme II).[3]

Scheme I



Scheme II



The susceptibility of the nitrene nitrogen to nucleophilic attack in these zerovalent compounds contrasts with the properties of more typical metal imido complexes, which are high oxidation state molecules with generally unreactive metal–nitrogen bonds.[4–6] Examples where electrophilic behavior is observed in such imido complexes are rare,[7] and pathways other than direct nucleophilic attack upon the nitrogen are often involved. For example, Brookhart and Templeton have reported the reaction of

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[1] (a) Sleiman, H. F.; Mercer, S.; McElwee-White, L. *J. Am. Chem. Soc.* **1989**, *111*, 8007–8009. (b) Arndtsen, B. A.; Sleiman, H. F.; Chang, A. K.; McElwee-White, L. *J. Am. Chem. Soc.* **1991**, *113*, 4871–4876. (c) Sleiman, H. F.; Arndtsen, B. A.; McElwee-White, L. *Organometallics* **1991**, *10*, 541–543. (d) Arndtsen, B. A.; Schoch, T. K.; McElwee-White, L. *J. Am. Chem. Soc.* **1992**, *114*, 7041–7047. (e) Fourquet, J. L.; Leblanc, M.; Saravanamuthu, A.; Bruce, M. R. M.; Bruce, A. E. *Inorg. Chem.* **1991**, *30*, 3241–3243. (f) Hegedus, L. S.; Kramer, A. *Organometallics* **1984**, *3*, 1263–1267. (g) Hegedus, L. S.; Lundmark, B. R. *J. Am. Chem. Soc.* **1989**, *111*, 9194–9198. (h) Pilato, R. S.; Williams, G. D.; Geoffroy, G. L.; Rheingold, A. L. *Inorg. Chem.* **1988**, *27*, 3665–3668. (i) Herndon, J. W.; McMullen, L. A. *J. Organomet. Chem.* **1989**, *368*, 83–101.

[2] (a) Schubert, U. *Advances in Metal Carbene Chemistry*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1989. (b) Weiss, K. In *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim, 1983; pp 227–246. (c) Dötz, K. H. *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 587–608. (d) Dötz, K. H. *New J. Chem.* **1990**, *14*, 433–445. (e) Brookhart, M.; Studabaker, W. B. *Chem. Rev.* **1987**, *87*, 411–432.

[3] (a) Kreissl, F. R.; Fischer, E. O.; Kreiter, C. G.; Fischer, H. *Chem. Ber.* **1973**, *106*, 1262–1276. (b) Fischer, H.; Fischer, E. O.; Kreissl, F. R. *J. Organomet. Chem.* **1974**, *64*, C41–C44. (c) Casey, C. P.; Polichnowski, S. W.; Shusterman, A. J.; Jones, C. R. *J. Am. Chem. Soc.* **1979**, *101*, 7282–7292. (d) Fischer, E. O.; Massböl, A. *Angew. Chem., Int. Ed. Engl.* **1964**, *2*, 580–581.

[4] For reviews on imido complexes, see: (a) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123–175. (b) Cenini, S.; LaMonica, G. *Inorg. Chim. Acta* **1976**, *18*, 279–293. (c) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley-Interscience; New York, 1988.

[5] Examples where nitrene transfer is observed include the following: (a) Walsh, P. J.; Baranger, A. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1992**, *114*, 1708–19. (b) Glueck, D. S.; Jianxin, W.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 2041–2054. (c) Mahy, J. P.; Bedi, G.; Battioni, P.; Mansuy, D. *J. Chem. Soc., Perkin Trans. 2* **1988**, 1517–1524. (d) Mansuy, D.; Mahy, J. P.; Dureault, A.; Bedi, G.; Battioni, P. *J. Chem. Soc., Chem. Commun.* **1984**, 1161–1163. (e) Groves, J. T.; Takahashi, T. *J. Am. Chem. Soc.* **1983**, *105*, 2073–2074. (f) Evans, D. A.; Faul, M. M.; Bilodeau, M. T. *J. Org. Chem.* **1991**, *56*, 6744–6746. (g) O'Connor, K. J.; Wey, S. I.; Burrows, C. J. *Tetrahedron Lett.* **1992**, *33*, 1001–1004.

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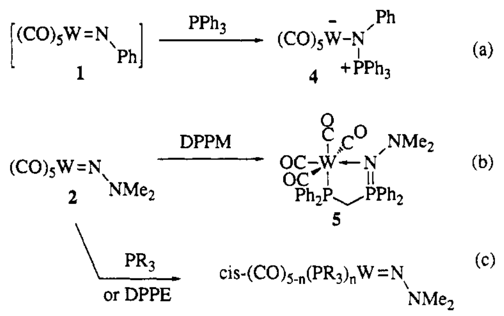
Scheme III



$[Tp'(CO)_2WNR]I$ (R = ^tBu, Ph) with $LiBH_4$ to generate the amido complexes $Tp'(CO)_2WNHR$. However, hydride attack occurs first upon a metal carbonyl, followed by migration.[8] Similarly, the formation of *N-tert*-butylaniline upon reaction of Ph_2Zn with $(Me_3SiO)_2Cr(N^tBu)_2$ may proceed via arylation of either the imido nitrogen or the metal center.[9] In addition to these, several metal imido complexes that are generated *in situ* have been reported to react electrophilically with olefins to generate *N*-tosyl- and *N*-triflylaziridines.[5c–g]

We now report that the zerovalent hydrazido (or donor-substituted nitrene) complex $(CO)_5W{=}NNMe_2$ (**2**) is capable of electrophilic behavior with bis(diphenylphosphino)methane (DPPM), in a reaction reminiscent of the addition of PPh_3 to $(CO)_5W{=}NPh$ (Scheme III). The metallacycle formed in this reaction (**5**) is sufficiently robust to be structurally characterized. This has allowed the comparison of the electrophilicity of this electron-rich hydrazido complex with that of the phenylnitrene species $(CO)_5W{=}NPh$ (**1**), as well as Fischer carbenes.

Results and Discussion

Products of Phosphine Addition to Zerovalent Nitrene Complexes. We have previously communicated that the transient $(CO)_5W{=}NPh$ (**1**) can be prepared by decomposition of zwitterionic complex **3**.[10,11] When **1** is generated in the presence of PPh_3, the phosphinimine complex $(CO)_5W(PhNPPh_3)$ (**4**) is formed (Scheme I).[1a] Complex **4** can be independently prepared by reaction of $(CO)_5W(THF)$ and $PhNPPh_3$, and its spectroscopic properties are in agreement with the zwitterionic structure shown in Scheme I. Most notably, the IR shows ν_{P-N} to be 803 cm^{-1}. This strongly suggests a single bond between phosphorus and nitrogen, similar to the ylides observed upon phosphine addition to Fischer carbenes.[1a] Both NMR and UV/vis kinetic experiments show that the disappearance of zwitterion **3** is first order in **3** and independent of phosphine concentration. This is consistent with the reaction pathway in Scheme I, where generation of the transient phenylnitrene complex $(CO)_5W{=}NPh$ (**1**) is followed by nucleophilic attack of phosphine upon the nitrene nitrogen to yield **4**.

Subsequent to this report, Bruce observed a similar product formed by migration of phosphine to nitrogen in a transient zerovalent molybdenum nitrene derived from addition of 8-azidoquinoline to $Mo(CO)_3(PPh_3)(CH_3CN)_2$.[1e] In a related reaction, free phosphinimines have been formed upon addition of phosphines to the high-valent imido complexes (TPP)Cr(NTol)[12] and $(Et_2dtc)_2MoO(NTs)$,[13] though intermediate phosphinimine complexes resulting from nucleophilic attack have not been seen in either system.

The formation of phosphinimine complex **4** by addition of PPh_3 to $(CO)_5W{=}NPh$ suggests a parallel between the phenylnitrene complex and non-heteroatom-substituted Fischer carbenes, which form similar adducts (Scheme IIa). However, the less electrophilic metal hydrazido complex $(CO)_5W{=}NNMe_2$ (**2**) had previously exhibited another mode of reactivity with phosphines. Addition of monodentate or ethano-bridged bidentate phosphines to **2** resulted in replacement of CO ligands to yield substituted hydrazido complexes (Scheme IIIc).[1d] Similar *cis* carbonyl replacements in heteroatom-stabilized Fischer carbenes have been shown to occur via a two-step mechanism where the first step is attack of phosphine at the electrophilic carbene carbon (Scheme IIb).[3a,b] In contrast, kinetic data on the substituion in **2** show the reaction rate to be independent of phosphine concentration, consistent with the rate-determining step being dissociation of CO and not phosphine attack on nitrogen.[1d]

It is now observed that the shorter chelating phosphine DPPM reacts with hydrazido complex **2** to generate a phosphinimine complex similar to **4**. Addition of 1 equiv of DPPM to a chloroform solution of **2** results in immediate effervescence from CO loss and a lightening of the reaction mixture to yellow. The ^1H NMR spectrum shows the quantitative transformation of **2** into **5** (Scheme IIIb). The dimethylamino group of **5** is shifted upfield to 2.0 ppm in the ^1H NMR spectrum,[14,15] suggesting a decrease in donation from the amino nitrogen into N_α of **5**. Such donation dominates the structure of the hydrazido ligand in **2**.[1d] The ^{13}C NMR spectrum contains three separate metal carbonyl signals in a 1:2:1 ratio, consistent with a *cis*-tetracarbonyl configuration, with one CO (211 ppm, $^2J_{P-C}$ = 34 Hz) showing the strong *trans* coupling to phosphorus, while the others (209 ppm, $^2J_{P-C}$ = 6.1 Hz; and 203, $^2J_{P-C}$ = 6.7 Hz) are located *cis* to DPPM. The ^{31}P NMR spectrum of **5** exhibits two signals,[16] one of which is strongly coupled to tungsten (18.5 ppm, $^1J_{W-P}$ = 240 Hz), while the other is not metal bound (42.4 ppm). The ^{13}C and ^{31}P NMR shifts are very similar to those reported for the related metallacycle $(CO)_4\overline{W[PPh_2CH_2PPh_2}NSiMe_3]$,[17a] as is the IR spectrum, which gives a P–N double bond stretch of 1110 cm^{-1}.

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(6) Many imido complexes undergo metathesis with aldehydes to yield imines: (a) Cotton, F. A.; Hall, W. T. *J. Am. Chem. Soc.* **1979**, *101*, 5094–5095. (b) Rocklage, S. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 7809–7811. (c) Rocklage, S. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 3077–3081.

(7) Nugent, W. A.; McKinney, R. J.; Kasowski, R. V.; Van-Catledge, F. A. *Inorg. Chim. Acta* **1982**, *65*, L91–3.

(8) (a) Luan, L.; Brookhart, M.; Templeton, J. L. *Organometallics* **1992**, *11*, 1433–1435. (b) Luan, L.; White, P. S.; Brookhart, M.; Templeton, J. L. *J. Am. Chem. Soc.* **1990**, *112*, 8190–8192.

(9) Nugent, W. A.; Harlow, R. L. *J. Am. Chem. Soc.* **1980**, *102*, 1759–1760.

(10) Prepared by the reaction of $(CO)_5W{=}C(OMe)Me$ and *cis*-azobenzene.[11]

(11) Sleiman, H. F.; McElwee-White, L. *J. Am. Chem. Soc.* **1988**, *110*, 8700–8701.

(12) TPP = tetraphenylporphyrinato. Elliott, R. L.; Nichols, P. J.; West, B. O. *Polyhedron* **1987**, *6*, 2191–2192.

(13) Et_2dtc = *N,N'*-diethyldithiocarbamate. Harlan, E. W.; Holm, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 186–193.

(14) Zerovalent tungsten hydrazido complexes of the form $(CO)_{5-n}(PR_3)_nW{=}NNMe_2$ typically have ^1H NMR resonances between 3.17 and 3.90 ppm.[1d]

(15) Donation of π electron density from the amino group into the nitrene nitrogen has been previously hypothesized to stabilize zerovalent tungsten hydrazido complexes.[1c,d]

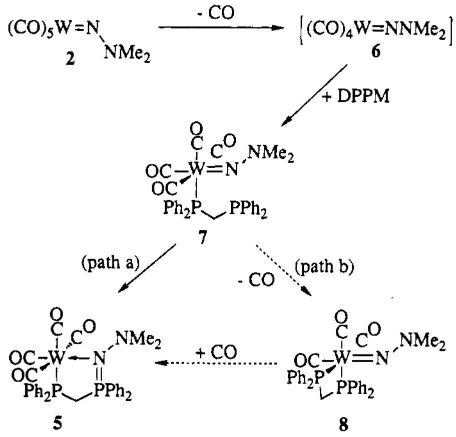
(16) All ^{31}P NMR values reported are referenced downfield of 85% H_3PO_4.

Table I. Kinetic Data for Reaction of 1 with DPPM[a]

[DPPM] (M)	equiv of DPPM	$k_{obs} \times 10^4$ (s^{-1})[b]
0.026	3.1	6.4
0.029	3.4	4.3
0.047	5.6	5.5
0.057	6.8	5.1
0.075	9.0	4.7
0.083	9.9	6.3

[a] Initial concentration of 1 = 0.0084 M, experiments performed at −20 °C. [b] Values ± 1.0.

Scheme IV



Kinetics of the Formation of 5. In order to elucidate the mechanism by which complex 5 is formed, kinetic experiments on the reaction of 2 with DPPM were performed at −20 °C and followed by ^1H NMR. These show the rate of disappearance of 2 to be first order in the concentration of 2 and independent of DPPM concentration (Table I). Such data strongly implicate a mechanism whose rate-determining step involves initial carbonyl loss to produce $(CO)_4W{=}NNMe_2$ (6) (Scheme IV). A similar reactive intermediate has been previously proposed in the reaction of 2 with monodentate phosphines.[1d] The DPPM-substituted complex 7 formed from 6 could then either undergo direct intramolecular nucleophilic attack upon the nitrene nitrogen (path a) or displace a second carbonyl to form 8, followed by CO-induced rearrangement to yield 5 (path b).

While our data are consistent with both mechanisms so long as the rate-determining step is 2 → 6, the stability of related hydrazido complexes with bidentate phosphine ligands[1d] suggests that once formed, 8 is unlikely to migrate a phosphine to nitrogen. In addition, the nitrene nitrogen of 7 should be more electrophilic than the nitrogen of bis(phosphine) 8.[18,19] For these reasons we favor the mechanism shown in path a, which involves nucleophilic attack of phosphine upon the nitrene nitrogen of hydrazido complex 7. The formation of 5 instead of the chelated complex 8 is likely a result of the shorter DPPM ligand not allowing 8 to adopt a stable octahedral geometry, as well as the stability of the five-membered metallacycle in 5. It should be noted that although there is no precedent for formation of the ring system in 5 by addition of a chelating phosphine to a metal nitrene or hydrazido complex, there are examples of similar cyclic structures formed from addition of DPPM to metal carbenes.[20]

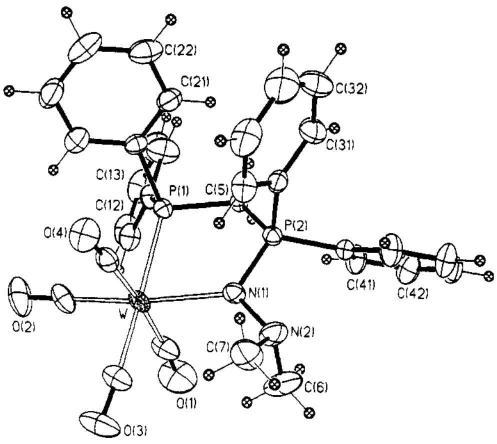


Figure 1. Molecular structure of 5. Selected bond distances (Å) and angles (deg) are the following: W–P(1), 2.486(2); W–N(1), 2.282(6); P(1)–C(5), 1.839(7); P(2)–C(5), 1.802(7); P(2)–N(1), 1.607(6); N(1)–N(2), 1.457(9); P(1)–W–N(1), 79.9(1); W–P(1)–C(5), 107.2(2); P(1)–C(5)–P(2), 110.6(4); C(5)–P(2)–N(1), 105.9(3); W–N(1)–P(2), 124.7(3); W–N(1)–N(2), 130.2(4).

Table II. Crystallographic Data

chemical formula	$C_{31}H_{28}N_2O_4P_2W$	*V*, Å^3	3011.8(11)
formula weight	738.3	*Z*	4
space group	$P2_1/n$	*T*, K	296
a, Å	10.797(3)	ρ_{calcd}, g cm^{-3}	1.628
b, Å	22.761(3)	μ (Mo Kα), cm^{-1}	40.58
c, Å	12.257(2)	*R*(*F*), %	3.87
β, deg	90.92(4)	*R*(*wF*), %	4.69

Crystal Structure of 5. Complex 5 can be isolated from the reaction mixture by precipitation with hexane. Recrystallization from CH_2Cl_2/hexane results in the formation of large yellow crystals. Identification of 5 as a phosphinimine complex was confirmed by X-ray crystallography (Table II). The ORTEP is shown in Figure 1, as well as important bond lengths and angles. Complex 5 has a pseudooctahedral geometry, with normal metal carbonyl and metal phosphine bond lengths. Both the relatively short P–N bond [1.607(6) Å][21,22] and long W–N bond [2.282(6) Å][23] are consistent with the σ-coordinated phosphinimine shown in resonance structure A. A similar geometry was found for the chelating ligand of the related complex $Cl_2Pd[PPh_2CH_2PPh_2NH]$,[17e] and the P–N bond distance is similar to what has been observed in other σ-coordinated phosphinimine complexes of late transition metals.[24a–f] This structure can be contrasted to the zwitterionic phosphinimine ligands (B) seen in early transition metal complexes, where the P–N bond length is expected to be ca. 1.8 Å.[24g]

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[17] For examples of 2-aza-3,5-phosphametallacyclopentenes, see: (a) Katti, K. V.; Cavell, R. G. *Organometallics* **1989**, *8*, 2147–2153. (b) Cavell, R. G.; Katti, K. V. *Phosphorus Sulfur* **1989**, *41*, 43–50. (c) Katti, K. V.; Cavell, R. G. *Phosphorus Sulfur* **1990**, *49–50*, 467–70. (d) Katti, K. V.; Cavell, R. G. *Organometallics* **1991**, *10*, 539–541. (e) Katti, K. V.; Batchelor, R. J.; Einstein, F. W. B.; Cavell, R. G. *Inorg. Chem.* **1990**, *29*, 808–814.

[18] Phosphines have been observed to be much weaker π electron acceptors than carbonyls.[19]

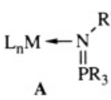
[19] (a) Wang, S. P.; Richmond, M. G.; Schwartz, M. *J. Am. Chem. Soc.* **1992**, *114*, 7595–7596. (b) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313–348.

[20] (a) Howard, J. A.; Jeffery, J. C.; Li, S.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1992**, 627–634. (b) Jeffery, J. C.; Li, S.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1992**, 635–640. (c) Brew, S. A.; Jenkins, P. D.; Jeffery, J. C.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1992**, 401–407.

[21] Typical P–N bond lengths are 1.78 Å for P–N and 1.64 Å for P=N.[22]

[22] (a) Abel, E. W.; Muckeljohn, S. A. *Phosphorus Sulfur* **1981**, *9*, 235–266. (b) Allcock, H. R. *Phosphorus-Nitrogen Compounds*; Academic Press: New York, 1972.

[23] Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1–S83.



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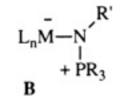

B

The structure of the phosphinimine moiety in **5** is quite different from that proposed previously for the related phosphine adduct of the phenylnitrene, $(CO)_5W(PhNPPh_3)$ (**4**). While complex **4** has not yet yielded crystals suitable for X-ray structure characterization, IR spectra can also be used to determine the P–N bond order in phosphinimine complexes as ν_{P-N} has characteristic values for single and double bonds.[24] The IR data support the assignment of a P–N double bond in **5** (1110 cm^{-1}) and a single bond in **4** (803 cm^{-1}).[25] The difference may be attributed to variations in the ancillary ligands of these molecules, as well as the cyclic structure of **5**. In the case of **4**, the five π-acidic metal carbonyl ligands may more easily stabilize a negative charge on the metal (B) relative to the phosphine-substituted metal in **5**. In addition, the electron-donating dimethylamino group in **5** may increase the electron density at N_α to where it can stabilize the positive charge at phosphorus by double bonding. While these changes are relatively small, the phosphinimine ligand appears sufficiently sensitive to alter the dominant resonance structure between **4** and **5**.

Comparison of the structural properties of **5** with those of the zerovalent hydrazido complex *fac*-$(CO)_3(DPPE)$-$W{=}NNMe_2$ (**9**)[1d] highlights some interesting electronic features of these complexes. Both the tungsten–nitrogen and nitrogen–nitrogen [1.457(9) Å] are elongated in **5** as compared to **9** [2.12(1) and 1.21(2) Å, respectively].[1d] This is an expected result from the removal of multiple bonding character of these bonds. Consistent with this is the rotation of the dimethylamino group in **5** perpendicular to the geometry required for conjugation with N(1). This π bonding has been previously hypothesized to be responsible for the stabilization of the electron-poor nitrene nitrogen of hydrazido complexes.[1c,d] In the case of **5**, this electron deficiency at N(1) is relieved by donation from the phosphine phosphorus into the former LUMO of **2**. The structural changes observed strongly support the electrophilicity of N_α in **9** and related hydrazido compounds. A more complete description of the electronic structure of d^6 tungsten hydrazido complexes is presented below.

Electronic Structure of Zerovalent Hydrazido Complexes. To further probe the novel electrophilic properties of these zerovalent hydrazido complexes, extended Hückel molecular orbital calculations[27] were performed on the model compound $(CO)_5W{=}NNH_2$ (**10**), and its constituent fragments $(CO)_5W$ and NH_2. The geometry for the hydrazido ligand was adapted from the crystal structure of **9**.[1d] Figure 2 contains the partial molecular orbital diagram resulting from these calculations. Orbital energy levels of the ambiphilic $(CO)_5W{=}NMe$ (**11**), which has been discussed elsewhere,[1b] have been included for comparison. The orbital interactions in **10** are very similar to those of the methyl-substituted nitrene **11**. The highest occupied molecular orbital (HOMO) of **10** is the π^* orbital resulting from the filled–filled interaction between the nitrene nitrogen lone pair (p_y/p_z) and the metal d_{yz}, while the lowest unoccupied molecular orbital (LUMO) is the perpendicular π^* orbital of the W–N double bond. Both of these molecular orbitals have significant coefficients at the nitrene nitrogen, suggesting that either nucleophilic or electrophilic reactions might occur at this site. As is anticipated for zerovalent nitrene complexes,[1b–d] the formal W–N bond order of both these complexes is 2, in contrast to the triple bond often seen with high oxidation state imido compounds.[4,28]

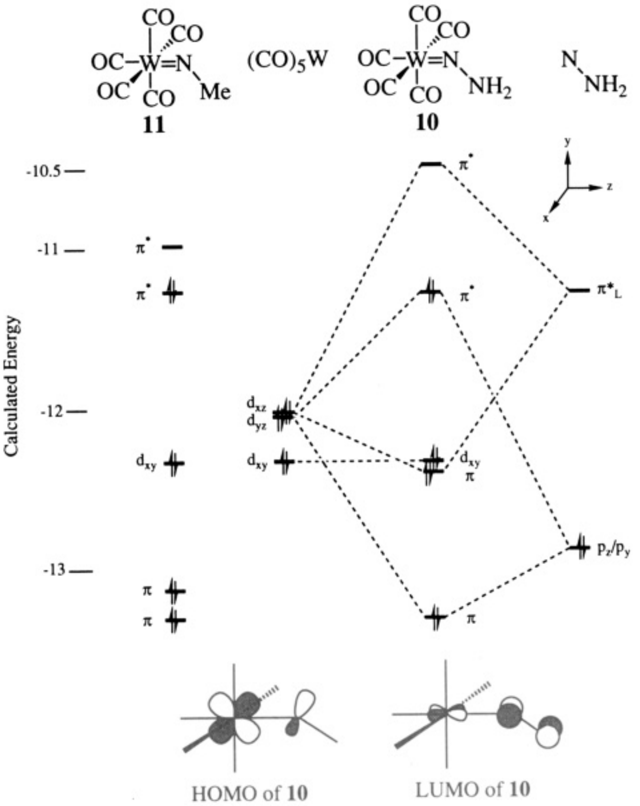

Figure 2. Orbital mixing diagram for the formation of **10** from the fragments $(CO)_5W$ and NNH_2. Energy levels and coefficients for **10** are from extended Hückel calculations described in the text. Energy levels for **11** are taken from ref 1b. (Orbitals of ancillary carbonyl ligands are omitted for clarity.)

The similarities of the HOMO's of **10** and **11** suggest that these complexes may exhibit similar nucleophilic properties, and indeed such behavior has been previously observed in the metathesis reactions of $(CO)_5W{=}NPh$ (**1**) and $(CO)_5W{=}NNMe_2$ (**2**) with electrophilic organic carbonyl compounds.[1b] On the other hand, π donation

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[24] Structural data for terminal metal phosphinimine complexes can be found in the following: (a) Dapporto, P.; Denti, G.; Dolcetti, G.; Ghedini, M. *J. Chem. Soc., Dalton Trans.* **1983**, 779–782. (b) Imhoff, P.; Elsevier, C. J.; Stam, C. H. *Inorg. Chim. Acta* **1990**, *175*, 209–216. (c) Cramer, R. E.; Roth, S.; Gilje, J. W. *Organometallics* **1989**, *8*, 2327–2330. (d) Vicente, J.; Chicote, M.-T.; Fernández-Baeza, J.; Lahoz, F. J.; López, J. A. *Inorg. Chem.* **1991**, *30*, 3617–3620. (e) Imhoff, P.; van Asselt, R.; Elsevier, C. J.; Zoutberg, M. C.; Stam, C. H. *Inorg. Chim. Acta* **1991**, *184*, 73–87. (f) Imhoff, P.; Nefkins, S. C. A.; Elsevier, C. J.; Goubitz, K.; Stam, C. H. *Organometallics* **1991**, *10*, 1421–1431. (g) Schrumpf, F.; Roesky, H. W.; Noltemeyer, M. *Z. Naturforsch.* **1990**, *45b*, 1600–1602.

[25] Typical metal bound phosphinimine double bond stretches[17,24] range from 1100 to 1300 cm^{-1}, while ylide-like single bonds[26] are below 975 cm^{-1}.

[26] (a) Dilworth, J. R.; de Liefde Meijer, H. J.; Teuben, J. H. *J. Organomet. Chem.* **1978**, *159*, 47–52. (b) Miller, J. S.; Visscher, M. O.; Caulton, K. G. *Inorg. Chem.* **1974**, *13*, 1632–1639. (c) Bock, H.; tom Dieck, H. *Z. Naturforsch.* **1966**, *21b*, 739–746.

[27] Extended Hückel calculations were carried out by using the program FORTICON8, obtained from QCPE as program QCMP001. Weighted H_{ij}'s were used, and the parameters for W were taken from the following: Kubacek, P.; Hoffman, R. *J. Am. Chem. Soc.* **1981**, *103*, 4320–4332.

[28] Based upon the 18-electron rule.[1b–d]

from the amino group has significantly raised the LUMO energy of 11 relative to 10. The experimental result of this is an expected decrease in electrophilicity in these hydrazido complexes relative to 2. The previously observed reaction of 2 with monodentate phosphines to displace a metal CO rather than add phosphine at nitrogen[1d] supports this hypothesis.

Since calculations have indicated that the replacement of a carbonyl with a PH_3 ligand *cis* to the nitrene does not significantly affect the frontier orbital energies,[29] the electronic structure of 7 should be similar to that of 2. Therefore, although electron donation from the amino group makes the LUMO less accessible than that of 2, electrophilic behavior in 2 is clearly possible. The structure of the DPPM adduct 5 demonstrates that nucleophilic attack of phosphines upon the nitrogen of the zerovalent hydrazido complex 7 can occur under certain conditions.

Conclusions

The reaction of 2 with DPPM demonstrates that electrophilic reactivity at nitrogen is general for zerovalent tungsten nitrene and hydrazido ligands and further supports the similarities between these complexes and their electrophilic carbon analogues, Fischer carbenes [$(CO)_5M{=}CRR'$, M = Cr, Mo, W]. Although addition of phosphines to 1 and 2 yields a phosphinimine complex in each case, the products exhibit significantly different phosphinimine bonding modes. Addition of DPPM to 2 to yield 5 in conjunction with the previously reported netathesis of 2 with carbonyl compounds[1b,c] demonstrates that 2 is ambiphilic, analogous to the behavior previously observed for $(CO)_5W{=}NPh$ (1).[1b] Extended Hückel calculations are in agreement with reaction of 2 as both a nucleophile and electrophile at N_α, which is to our knowledge novel for a transition-metal hydrazido complex.

Experimental Section

General. Standard inert atmosphere techniques were used in all of these experiments. Diethyl ether and toluene were distilled from sodium/benzophenone. Hexane, petroleum ether, *n*-pentane, chloroform, and methylene chloride were distilled from CaH_2. All NMR solvents were degassed by three freeze–pump–thaw cycles. Benzene-d_6 and toluene-d_8 were vacuum transferred from sodium/benzophenone. $CDCl_3$ and CD_2Cl_2 were stored over 3-Å molecular sieves. All other reagents were purchased in reagent grade and used with no further purification.

^1H, ^{13}C, ^{15}N, and ^{31}P NMR spectra were recorded on a Varian XL-400 NMR spectrometer. IR spectra were recorded on a Perkin-Elmer 1600 spectrometer. Mass spectra were obtained at the University of California, San Francisco, CA.

Unless otherwise stated, all photolyses were performed in 5-mm NMR tubes or 5-mL test tubes by irradiation with a Hanovia medium-pressure mercury vapor lamp in a Pyrex immersion well.

$(CO)_5WNPhNPhC(OMe)Me$ (3)[1b] and $(CO)_5W(THF)$[30] were prepared by literature methods. $(CO)_5W{=}NNMe_2$ (2)[1b] was prepared as reported previously and used in situ based upon a calculated yield of 65%.

Decomposition of 3 in the Presence of PPh_3. To a 0.5-mL toluene-d_8 solution of zwitterion 3 (31 mg, 0.05 mmol) was added an excess of triphenylphosphine (58 mg, 0.11 mmol). The solution was photolyzed at room temperature with Pyrex-filtered light. After 3 h, ^1H NMR indicated the complete disappearance of 3 and the quantitative formation of $(CO)_5W(PhNPPh_3)$ (4). 4 was identified by comparison of spectral data to that of an authentic sample (see below). Yields for the thermal reaction (ca. 14 h at room temperature) were similar.

Synthesis of $(CO_5W(PhNPPh_3)$ (4). $W(CO)_6$ (153 mg, 0.44 mmol) was dissolved in 50 mL of THF and loaded into a photolysis reactor. The solution was photolyzed for 1.5 h under a flow of nitrogen and then transferred into a flask containing $PhN{=}PPh_3$ (118 mg, 0.33 mmol). After 30 min the solution turned light brown. The solvent was removed in vacuo and the residue dissolved in 5 mL of $CHCl_3$. Following filtration, the solution was added to 10 mL of cold methanol, and the mixture was cooled. Yellow crystals of 4 (65.3 mg) formed in 38% yield: ^1H NMR ($CDCl_3$) δ 6.84 (t, 1H), 6.92 (d, 2H), 7.07 (t, 2H), 7.48 (m, 6H), 7.61 (m, 9H); ^{31}P NMR (C_6D_6) δ 31.2 (s); IR (KBr) 2060, 1966, 1909, 1866 (ν_{CO}), 803 (ν_{PN}) cm^{-1}; MS (FAB) M^+ 677 (isotope abundance pattern matched simulation for $C_{29}H_{20}NO_5PW$).

Kinetics of Decomposition of 3 with PPh_3. Zwitterion 3 (19 mg, 0.043 mmol) was dissolved in 1 mL of toluene-d_8. Half of the solution was transferred to a separate NMR tube, and 5 equiv of PPh_3 (44 mg, 0.17 mmol) was added. The disappearance of 3 was monitored by ^1H NMR every hour over 14 h. The rates of decomposition of 3 were identical within experimental error (ca. 5%).

Synthesis of $(CO)_4\overline{W[PPh_2CH_2PPh_2N}NMe_2]$ (5). To a 10-mL $CDCl_3$ solution of $(CO)_5W{=}NNMe_2$ (2) (25 mg, 0.062 mmol) was added bis(diphenylphosphino)methane (24 mg, 0.062 mmol). The solution immediately turned yellow, and there was effervescence. ^1H NMR showed the quantitative formation of 5. Concentration of the solution to 1 mL, addition of 20 mL of hexane, and storage at −40 °C for 12 h resulted in precipitation of a yellow powder of 5 (40 mg, 0.054 mmol) in 87% yield. Recrystallization from CH_2Cl_2/hexane gave yellow crystals of 5: ^1H NMR ($CDCl_3$) δ 2.02 (s, 6H, $N(CH_3)_2$), 3.20 (t, 2H, CH_2), 7.2–7.8 (m, 20H, Ph); ^{13}C NMR ($CDCl_3$) δ 210.9 (d, $^2J_{PC} = 34$ Hz), 209.5 (t, $^2J_{PC} = 6.1$ Hz), 203.2 (d, $^2J_{PC} = 6.7$ Hz); ^{31}P NMR ($CDCl_3$) 18.5 (d, $^2J_{PP} = 46$ Hz, $^1J_{WP} = 240$ Hz), 42.4 (d, $^2J_{PP} = 46$ Hz); IR (CH_2Cl_2) 2002, 1889, 1873 (ν_{CO}) cm^{-1}.

Kinetics of Reaction of 2 with DPPM. To separate NMR tubes containing a 0.5-mL $CDCl_3$ solution of 2 (0.004 mmol) at −60 °C was added 3.1 equiv (5 mg, 0.013 mmol), 5.6 equiv (9 mg, 0.023 mmol), and 8.7 equiv (14 mg, 0.036 mmol) of DPPM. The solutions were warmed to −20 °C in the NMR probe, and the disappearance of 2 was monitored every 4 min for 30 min. The plot of ln [2] vs time gave a straight line with a slope equal to k_{obs}. The reactions were repeated on a separate occasion with 3.4 equiv (5.5 mg, 0.014 mmol), 6.8 equiv (11 mg, 0.028 mmol), and 9.9 equiv (16 mg, 0.041 mmol) of DPPM. Error in k_{obs} is based upon 5% NMR integration error.

Crystal Structure of 5. The diffractomer used for data collection was a Siemens PR equipped with Mo radiation. Crystallographic data are collected in Table II. A sample affixed to a glass fiber was found from photographic evidence to possess 2/m Laue symmetry. From systematic absences in the diffraction data the space group was uniquely assigned. Correction for absorption was applied by standard empirical methods. The W atom was found from a Patterson map. All non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were included as idealized isotropic contributions. All computations used the SHELXTL-PC library of routines and databases (G. Sheldrick, Siemens, Madison, WI).

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Supplementary Material Available: Tables of bond distances and angles, hydrogen atom coordinates, and the thermal parameters (9 pages). Ordering information is given on any current masthead page.

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