(chromium trioxide, 0.022 mol, and sulfuric acid, 30 mL, 4 M) is added dropwise to the reaction flask (in the case of cyclopropylmethyldiazirine, 0.022 mol of freshly prepared silver oxide is substituted). After 30 min the cooling bath is removed from the reaction flask, allowing the volatile diazirine to be eluted with the carrier gas (Ar), and the diazirine is collected into the pentane. The diazirines are identified by their characteristic UV spectrum: All diazirines synthesized had $\lambda_{max} = 364$ nm in pentane except dimethyldiazirine-d_6, for which $\lambda_{max} = 362$ nm.

NMR Analysis of Photolyzed Diazirine–Methanol Solutions. The yields of dimethylcarbene-d_6 and dimethylcarbene were measured by analyzing the products of photolysis of methanolic solutions of the diazirines, by NMR spectroscopy. The diazirines were prepared in methanol and methanol-d_4, respectively; a small amount of benzene-d_6 (or benzene) was added as an internal standard. Two peaks are found in the initial ^{2}H-NMR spectrum of dimethyldiazirine-d_6; benzene-d_6 (δ 7.15), and dimethyldiazirine-d_6 (δ 0.749). A third peak appears after 12 h of photolysis at 350 nm (Rayonet) at 4 °C, which is attributed to the insertion product (δ 0.880). When integration against the benzene standard is carried out, we find an ~52 ± 8% yield of carbene insertion product (isopropyl-d_6 methyl ether). The spectra for dimethyldiazirine can be analyzed in the same manner, showing a 40 ± 5% yield of carbene insertion product (isopropyl methyl-d_3 ether).

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Registry No. 1, 136863-30-4; D_2, 7782-39-0; 3,3-dimethyldiaziridine, 5161-49-9; dimethylcarbene, 40852-89-9; cyclopropyl(methyl)diaziridine, 141784-28-3; isopropyl(methyl)diaziridine, 141784-29-4; *tert*-butyl(methyl)diaziridine, 141784-30-7; dimethyldiaziridine, 20686-76-4.

Stabilization of Zero-Valent Hydrazido Complexes by Phosphine Ligands. Crystal Structure of *fac*-$(CO)_3(DPPE)W{=}NNMe_2$, a Nitrene Analogue to Fischer Carbenes

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Abstract: The zero-valent tungsten hydrazido complex $(CO)_5W{=}NNMe_2$ (**2**) reacts with phosphines or phosphites to form *cis*-$(CO)_n(PR_3)_{5-n}W{=}NNMe_2$ (**3**, **8**, and **10**). Spectroscopic data show that these complexes contain bent hydrazido ligands, as does **2**. Kinetics are consistent with substitution of CO by PR_3 via a dissociative process. Complexes **3**, **8**, and **10** are significantly more stable than **2**, with *fac*-$(CO)_3(DPPE)W{=}NNMe_2$ (**10b**) [DPPE = 1,2-bis(diphenylphosphino)ethane] being isolable as a crystalline solid. Complex **10b** was characterized by X-ray crystallography: $P2_1/n$; $a = 8.4406$ (20) Å, $b = 23.9747$ (57) Å, $c = 16.5073$ (41) Å, $\beta = 92.36$ (2)°, $V = 3337.6$ (25) Å^3, $Z = 4$, $R(F) = 6.3\%$, $R(wF) = 7.2\%$, for 3025 reflections, $F_o > 3\sigma(F_o)$.

Introduction

The generation of zero-valent transition metal nitrene[1,2] (or imido) and hydrazido[3] complexes of the form $L_5M{=}NR$ (**1**) has been the subject of several reports in recent years, but in all cases these compounds have proven too labile for isolation.[1-3] Interest in the preparation of such complexes arises to an extent from their potential to serve as nitrene (NR) transfer agents. Their carbon analogues, Fischer carbenes [$(CO)_5M{=}CRR'$, M = Cr, W], have been observed to undergo a rich variety of transformations involving the incorporation of the carbene moiety into various organic products. Examples include ring annelations,[4] olefin cyclopropanation,[5] and various metathesis reactions.[6]

Systems in which metal nitrene complexes exhibit reactivity parallel to that of Fischer carbenes are rare. Bergman has shown that the imido ligand of Cp*IrN^{t}Bu undergoes a variety of cyclization reactions with unsaturated substrates, including incorporation of the N^{t}Bu fragment into a substituted pyrrole upon reaction with dimethyl acetylenedicarboxylate.[7] There are also several reports in which transition metal nitrene complexes have been proposed to be the reactive species for the transformation of olefins into *N*-tosyl- or *N*-triflylaziridines.[8] In addition to these, many high oxidation state imido complexes undergo metathesis with aldehydes to form imines, a reaction driven by the stability

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Table I. Spectroscopic Data for *cis*-$\mathrm{PR_3(CO)_4W{=}NNMe_2}$ (**3a–e**)

complex ($\mathrm{PR_3}$)	^{1}H NMR[a] (δ)	^{13}C NMR (δ)	^{15}N NMR[b] (δ)	^{31}P NMR[c] (δ)	IR[d] (cm^{-1}) ν_{WCO}	$\Delta G^{\ddagger}$(N–N)[e]
3a $\mathrm{PPh_3}$	3.49 (s, 6 H)	223.6 (d, $^2J_{\mathrm{PC}} = 5.2$ Hz) 208.2 (d, $^2J_{\mathrm{PC}} = 30$ Hz) 203.3 (d, $^2J_{\mathrm{PC}} = 6.2$ Hz) 59.8 (s)	418.8 (s)	23.62 ($^1J_{\mathrm{WP}} = 246$ Hz) (d, $^2J_{\mathrm{NP}} = 4.3$ Hz)[g]	2004 m[f] 1870 s	8.4 kcal/mol ($T_c = -98$ °C)[h] $\Delta\nu = 47$ Hz
3b $\mathrm{PMe_3}$	3.78 (s, 6 H) 1.51 (d, 9 H $^2J_{\mathrm{PH}} = 8$ Hz)	224.3 (s) 210.1 (d, $^2J_{\mathrm{PC}} = 25$ Hz) 202.8 (s) 60.2 (s)	422.6 (d, $^2J_{\mathrm{PN}} = 8.1$ Hz)	−28.15 ($^1J_{\mathrm{WP}} = 242$ Hz)	2009 m 1903 s 1884 s 1856 s	9.0 kcal/mol ($T_c = -92$ °C) $\Delta\nu = 26$ Hz
3c $\mathrm{PCy_3}$	3.77 (s, 6 H)	225.0 (d, $^2J_{\mathrm{PC}} = 5.2$ Hz) 208.8 (d, $^2J_{\mathrm{PC}} = 29$ Hz) 205.0 (d, $^2J_{\mathrm{PC}} = 6.4$ Hz) 60.0 (s)	427.9 (s)	32.14 ($^1J_{\mathrm{WP}} = 235$ Hz)	2012 m 1925 s	8.4 kcal/mol ($T_c = -104$ °C) $\Delta\nu = 22$ Hz
3d $\mathrm{P(OMe)_3}$	3.78 (s, 6 H) 3.65 (d, 9 H $^3J_{\mathrm{PH}} = 11$ Hz)	220.1 (d, $^2J_{\mathrm{PC}} = 7.8$ Hz) 205.8 (d, $^2J_{\mathrm{PC}} = 47$ Hz) 200.9 (d, $^2J_{\mathrm{PC}} = 10$ Hz) 60.1 (s)	413.2 (s)	145.1 ($^1J_{\mathrm{WP}} = 393$ Hz)	2022 m 1924 s 1896 s 1869 s	8.9 kcal/mol ($T_c = -88$ °C) $\Delta\nu = 48$ Hz
3e $\mathrm{P(OPh)_3}$	3.33 (s, 6 H)	217.8 (d, $^2J_{\mathrm{PC}} = 8.6$ Hz) 204.7 (d, $^2J_{\mathrm{PC}} = 56$ Hz) 200.1 (d, $^2J_{\mathrm{PC}} = 9.5$ Hz) 59.8 (s)	414.6 (s)	130.9 ($^1J_{\mathrm{WP}} = 423$ Hz)	2043 m 1953 s 1929 s	9.1 kcal/mol ($T_c = -88$ °C) $\Delta\nu = 73$ Hz

[a] NMR taken in $\mathrm{CDCl_3}$. [b] Values referenced to $\mathrm{CH_3NO_2}$ at 0 ppm. [c] Reference to 85% $\mathrm{H_3PO_4}$ in $\mathrm{H_2O}$. [d] Values taken in $\mathrm{CH_2Cl_2}$. [e] NMR in $\mathrm{CD_2Cl_2}$. [f] KBr pellet. [g] With α-^{15}N label complex. [h] Coalescence temperature of dimethylamino signal.

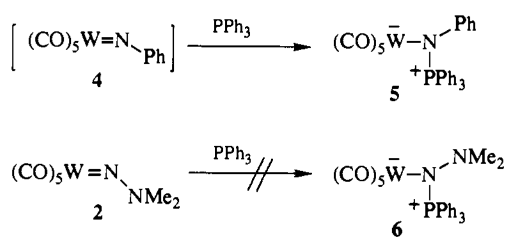
of the high-valent oxo complex formed.[9]

The scarcity of reported reactions between metal imido complexes and organic substrates is striking given the number of these compounds.[10] This may be a consequence of the high oxidation state of the metal in nearly all these complexes. In high-valent imido complexes, the nitrogen lone pair is generally donated into an empty metal d orbital, creating a linear and often unreactive metal nitrogen triple bond.[10a] Isolable imido or hydrazido complexes in any low oxidation state are very uncommon. To our knowledge, there are only three structurally characterized complexes of this type. Two of these, the reactive $\mathrm{Cp^*Ir{\equiv}NR}$[7] discussed above and $\mathrm{Fe(porphyrin)NNC_9H_{18}}$,[11] contain linear imido and hydrazido ligands, respectively. The third, $\mathrm{Cp(CO)_2Re{=}NNMe[}p\mathrm{\text{-}C_6H_4OMe]}$,[12] provides a rare example of a strongly bent hydrazido ligand.

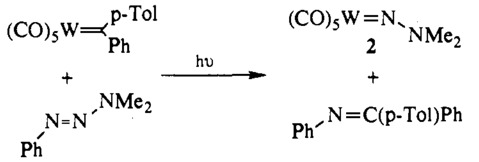
In contrast to high-valent transition metal imido and hydrazido complexes, the zero-valent nitrene complexes $\mathrm{L_5W{=}NR}$ are predicted to possess a bent, doubly bonded nitrene ligand, as donation of the nitrogen lone pair into the electron rich metal center would result in a 20 e$^-$ complex.[13,14] This situation is analogous to that leading to the bent ligand in the Re hydrazido complex described above.[12]

In the bent complexes, the nitrene or hydrazido ligand can be considered a neutral 2 e$^-$ donor. Thus, these $\mathrm{L_5W{=}NR}$ species should more closely resemble the zero-valent Fischer carbenes than the linear imido complexes. They would then appear to be excellent candidates to mimic the reactivity of the carbenes and there are indeed certain parallels between the behavior of the $\mathrm{(CO)_5W{=}NR}$ species and that of Fischer carbenes.[1c,3] However, the features that make these complexes reactive at the metal–nitrogen bond have also rendered them too labile to isolate.[1,2]

Scheme I



We recently reported the preparation of $\mathrm{(CO)_5W{=}NNMe_2}$ (**2**) by photochemical metathesis of $\mathrm{(CO)_5W{=}Ph(Tol)}$ and $\mathrm{PhN{=}NNMe_2}$ (eq 1).[3] This complex shows greatly increased stability as compared to the previously reported arylnitrene complexes,[1,2] persisting in solution at room temperature for several hours. Spectroscopic data for **2** demonstrate it to contain a bent $\mathrm{NNMe_2}$ ligand, with significant donation of electron density from the amino group into the nitrene nitrogen. This stabilization by electron-donating substituents is analogous to that observed with Fischer carbenes, where those that bear heteroatom-containing substituents are much more stable than those with only aryl or alkyl groups.[15] Since complex **2** is formally a hydrazido complex it will be referred to as such here; however, we propose that it is more descriptive to consider complexes such as **2** as donor-substituted nitrene complexes, in analogy to the Fischer carbenes.



(1)

We now report that complex **2** undergoes reaction with phosphines, leading to the replacement of one or more of the metal carbonyls (eq 2). The $\mathrm{PR_3}$-substituted hydrazido complexes exhibit even greater stability than the parent compound **2**. This has led to the first isolation and structural characterization of a tungsten(0) hydrazido complex, *fac*-$\mathrm{(CO)_3(DPPE)W{=}NNMe_2}$.

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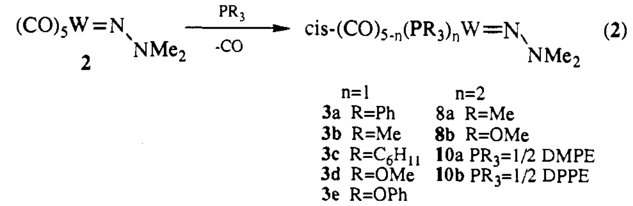


(2)

Results and Discussion

Reaction of 2 with Monodentate Phosphines. The addition of 1 equiv of PR$_3$ (R = aryl, alkyl, OR) to a chloroform solution containing (CO)$_5$W=NNMe$_2$ (**2**)[1c] results in an immediate effervescence and darkening of the reaction mixtures. The ^{1}H NMR spectra reveal the disappearance of **2** and the formation of a new series of compounds (**3a–e**) (eq 2). Complexes **3a–e** have been identified as *cis*-(PR$_3$)(CO)$_4$W=NNMe$_2$, based on the data below.

The transient nitrene complex (CO)$_5$W=NPh (**4**) has been shown to undergo nucleophilic attack by PPh$_3$ to yield phosphinimine complex **5**, which releases the free phosphinimine Ph$_3$P=NPh upon treatment with additional CO[1b] (Scheme I). A similar addition of PPh$_3$ to the nitrene nitrogen in **2** would result in formation of (CO)$_5$W(Ph$_3$P=NNMe$_2$) **6** or the free aminophosphinimine Ph$_3$P=NNMe$_2$ (**7**). Therefore, an authentic sample of phosphinimine **7** was prepared and reacted with (CO)$_5$W(THF)[16] to produce the phosphinimine complex **6**. Multinuclear NMR spectra of **6** and **7** confirm that neither one is **3a**, the product of the reaction of **2** with PPh$_3$.

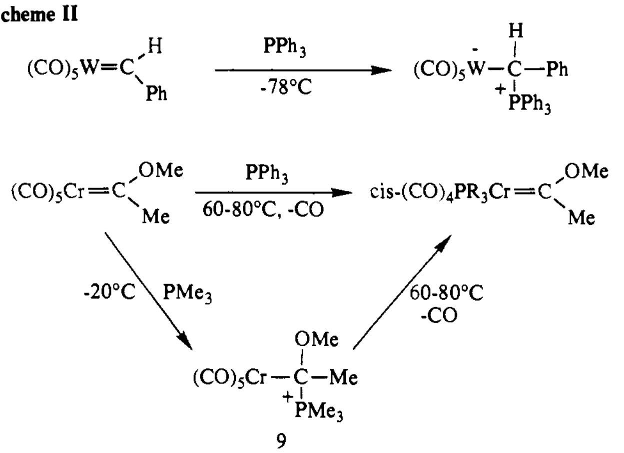
Spectroscopic data for **3a–e** are summarized in Table I. In their ^{1}H NMR spectra, the dimethylamino signal of each is upfield from that of **2** (3.90 ppm). In addition, there is a PR$_3$ signal which integrates to one PR$_3$ per dimethylamino group. The ^{31}P NMR spectra of **3a–e** provide strong evidence for the coordination of the PR$_3$ ligand to the metal center. As can be seen in Table I, **3a–e** all have one phosphorus signal with the expected $^1J_{P-W}$ (242–423 Hz).[17]

The ^{13}C NMR data of **3a–e** are also consistent with the coordination of a single phosphine cis to the hydrazido ligand. Compounds **3a–e** all possess three inequivalent CO peaks in a 1:2:1 ratio. Such a pattern is indicative of the replacement of one carbonyl of **2** with a PR$_3$ unit. The substitution of the *trans*-CO can be ruled out, since all four CO's in *trans*-PR$_3$(CO)$_4$W=NNMe$_2$ are expected to be equivalent. In addition, one of the carbonyl signals for **3a–e** shows the large $^2J_{P-C}$ typical for a carbonyl trans to phosphine.[17] The IR spectra of **3a–e** all show ν_{MCO} patterns consistent with *cis*-PR$_3$(CO)$_4$W=NNMe$_2$ complexes.

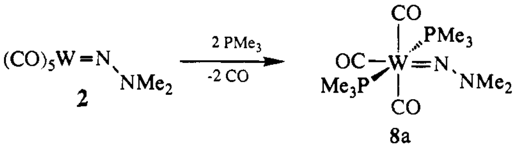
In the characterization of **2**, ^{15}N NMR was used to help ascertain the geometry of the hydrazido ligand. The dramatic shift of the NMR signal of the nitrene nitrogen (N$_\alpha$) to 420 ppm downfield of CH$_3$NO$_2$ was taken as evidence for bending at N$_\alpha$.[3] When **3a–e** were prepared from **2** which was ^{15}N labeled at N$_\alpha$, they all exhibited similar deshielding in the ^{15}N NMR, with peaks between 413 and 428 ppm. In the case of **3b**, the coupling between phosphorus and nitrogen was strong enough for the signal to be split into a doublet ($^2J_{P-N}$ = 8.1 Hz). The geometry of the hydrazido ligand in these complexes thus appears to be very similar to that of **2**.

To further probe the nature of the hydrazido ligand, variable-temperature ^{1}H NMR studies were performed on **3a–e**. In all cases, the room temperature NMR showed a sharp singlet at 25 °C for the dimethylamino group which upon cooling broadens and eventually is resolved into two distinct signals in a 1:1 ratio. The phosphine ^{1}H NMR signals remained unchanged at all temperatures. This behavior is interpreted as arising from partially restricted rotation about the N–N bond of the hydrazido ligand, similar to that observed in **2**.[2] The coalescence temperatures for **3a–e** were in the range of −88 to −104 °C, which gives an estimate of their barrier of rotation (ΔG^*) of 8.4–9.1 kcal/mol.[18]

Scheme II



In the cases of **3a**, **3c**, and **3e**, the addition of excess phosphine or phosphite did not result in further carbonyl substitution. The addition of 2 equiv of trimethylphosphine to **2**, however, leads to the production of another compound **8a**, which has been identified as *trans,mer*-(CO)$_3$(PMe$_3$)$_2$W=NNMe$_2$ (eq 3). When greater than 1 equiv of P(OMe)$_3$ is added to **2**, a similar reaction occurs to produce **8b**, but the reaction invariably forms mixtures of **8b** and **3d** as well as other decomposition products.



(3)

The ^{1}H NMR spectra of **8a** and **8b** (Table II) each show a dimethylamino singlet upfield of those for **3b** and **3d**, respectively, and one phosphine (or phosphite) doublet. Integration of the signals indicates that there are two phosphines per NMe$_2$ unit. The ^{31}P NMR spectra of **8a** and **8b** each have only one signal, which shows coupling to tungsten similar to that seen in the monosubstituted complexes. This shows that the phosphorus-containing ligands are chemically equivalent, and therefore both cis to the hydrazido fragment.

The meridional orientation of the carbonyls in **8a,b** is shown by the ^{13}C NMR data. There are two carbonyl peaks in a 2:1 ratio in the spectra for both complexes, with the larger of the two signals split into a triplet. This eliminates a facial conformation of **8a,b**, since it would give rise to a doublet of doublets for the cis carbonyls, due to stronger trans coupling to phosphorus.

^{15}N NMR spectra of **8a,b** labeled at the nitrene nitrogen once again exhibit one signal shifted very far downfield. In addition, **8a** shows the nitrogen–phosphorus coupling that is observed in **3b**, this time splitting the signal into a triplet ($^2J_{P-N}$ = 8.1 Hz).

Mechanism of Carbonyl Substitution in 2. The formation of the phosphine-substituted hydrazido complexes **3a–e** and **8a,b** via reactions of PR$_3$ with **2** illustrates the dramatic shift of reactivity in going from (CO)$_5$W=NPh (**4**), which forms phosphinimine complex **5** upon reaction with PPh$_3$ (Scheme I), to the donor-stabilized (CO)$_5$W=NNMe$_2$. The observation of restricted rotation about the N–N bond in **2**[3] indicates substantial donation of electron density to the nitrene nitrogen. Such donation makes N$_\alpha$ of **2** less susceptible to attack by nucleophiles and therefore formation of a phosphinimine complex such as **6** is suppressed.

The substituent effect upon the reactivity of these nitrene complexes invites further comparison with their carbon analogues. Alkyl- or aryl-substituted Fischer carbenes are known to react

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[18] The rate constant for the exchange was calculated by using $k = (\pi)\Delta\nu/2^{1/2}$ at the coalescence temperature.[19]

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Table II. Spectroscopic Data for $(PR_3)_2(CO)_3W{=}NNMe_2$ (**8a**,**b** and **10a**,**b**)

complex (PR_3)	^{1}H NMR[a] (δ)	^{13}C NMR (δ)	^{15}N NMR[b] (δ)	^{31}P NMR[c] (δ)	IR[d] (cm^{-1}) ν_{WCO}	$\Delta G^{\ddagger}$(N–N)[e]
8a PMe_3	3.67 (s, 6 H) 1.37 (d, 18 H, $^2J_{PH}$ = 6 Hz)	237.0 (s) 216.9 (t, $^2J_{PC}$ = 14 Hz) 58.6 (s)	427.4 (t, $^2J_{PN}$ = 8.0 Hz)	−30.09 ($^1J_{WP}$ = 265 Hz)	1919 s 1823 s 1797 s	9.5 kcal/mol (T_c = −88 °C)[f] $\Delta\nu$ = 20 Hz
8b $P(OMe)_3$	3.72 (s, 6 H) 3.67 (d, 18 H $^3J_{PH}$ = 11 Hz)	228.3 (t, $^2J_{PC}$ = 7.5 Hz) 203.6 (t, $^2J_{PC}$ = 10 Hz) 59.5 (s)	423.0 (s)	147.2 ($^1J_{WP}$ = 387 Hz)	1945 s 1862 sh 1839 s	g
10a DMPE	3.62 (s, 6 H) 1.70 (m, 4 H) 1.59 (d, 6 H, $^2J_{PH}$ = 7 Hz) 1.19 (d, 6 H, $^2J_{PH}$ = 7 Hz)	235.9 (s) 218.3 (dd $^2J_{PC(cis)}$ = 6 Hz, $^2J_{PC(trans)}$ = 34 Hz) 58.8 (s) 30.2 (t, J_{PC} = 20 Hz)	422.3 (t, $^2J_{PN}$ = 7.8 Hz)	14.01 ($^1J_{WP}$ = 228 Hz)	1916 s 1818 s	T_c < −107 °C
10b DPPE	3.17 (s, 6 H) 2.71 (m, 2 H) 2.60 (m, 2 H)	233.7 (s) 217.4 (dd, $^2J_{PC(cis)}$ = 6 Hz, $^2J_{PC(trans)}$ = 35 Hz) 58.4 (s) 27.2 (t, J_{PC} = 18 Hz)	425.6 (s)	39.2 ($^1J_{WP}$ = 229 Hz)	1908 s[h] 1814 s 1803 s	8.8 kcal/mol (T_c = −76 °C) $\Delta\nu$ = 292 Hz

[a] NMR taken in $CDCl_3$. [b] Values referenced to CH_3NO_2 at 0 ppm. [c] Reference to 85% H_3PO_4 in H_2O. [d] Values taken in CH_2Cl_2. [e] NMR in CD_2Cl_2. [f] Coalescence temperature of dimethylamino peak. [g] Interference from $P(OMe)_3$ and decomposition peaks prevented determination of value. [h] KBr pellet.

Table III. Kinetic Data for Reaction of **2** with PR_3[a]

PR_3	[PR_3] (M)	10^4k_{obs} (s^{-1})[b]
PPh_3	0.022	3.2
	0.062	4.1
	0.12	3.8
$P(OPh)_3$	0.032	3.8

[a] Initial concentration of **2** was 0.020 M, experiments performed at −20 °C. [b] Values ±0.5.

immediately with phosphines to form ylides,[15a] while the less electrophilic heteroatom-stabilized carbenes react at 60–80 °C to replace a metal carbonyl with PPh_3 (Scheme II).[20a]

In the case of the Fischer carbenes, substitution of PMe_3 for CO proceeds through phosphine ylide **9**[20b] (Scheme II). To investigate whether a similar intermediate was formed in the conversion of **2** to **3a–e**, the formation of **3a** and **3b** was monitored by low-temperature ^{1}H NMR. While at temperatures below −20 °C the reaction could be slowed enough to observe the disappearance of **2**, in neither case could an intermediate be detected. Subsequent ^{1}H NMR kinetic experiments on the reaction of **2** with PPh_3 and $P(OPh)_3$ showed a first-order disappearance of **2** with no dependence on phosphine concentration, and no rate difference between the different phosphorus ligands (Table III). Thus, in contrast to carbene complexes, this reaction appears to proceed via a dissociative process. The dissociation of CO from **2** is greatly accelerated ($t_{1/2}$ = 30 min at −20 °C) as compared to that of the Fischer carbene $(CO)_5W{=}C(OMe)Ph$ ($t_{1/2}$ = 8.3 h at 77 °C).[21] This enhanced CO labilization in **2** can be explained by the ability of the hydrazido ligand to act as a 4-electron donor (which the carbene ligand cannot do), thereby stabilizing the five-coordinate intermediate. This type of dissociative mechanism is not at all uncommon for octahedral carbonyl complexes containing donor ligands.[22]

During substitution of phosphines for carbonyls in the Fischer carbenes, the phosphine first coordinates cis to the carbene ligand and then the complex rearranges to the more stable trans isomer.[23] In contrast, we have seen no evidence for the isomerization of **3a–e** to their trans isomers, even at elevated temperatures.

Stabilization of 3 and 8 by Phosphine Ligands. While the spectroscopic data for **3** and **8** seem to indicate these complexes have hydrazido ligands that are structurally similar to that of **2**, the phosphine-substituted complexes exhibit increased stability. As has been reported, $(CO)_5W{=}NNMe_2$ decomposes immediately upon concentration of the reaction solution, yielding no identifiable products.[3] The phosphine-substituted hydrazido complexes **3a–e** and **8a**,**b**, however, do survive concentration and redilution of the solution, though there is some decomposition. This increased stability has led to the partial purification of complexes **3a**, **3c**, and **3e** by precipitating them out of solution as black powders upon addition of hexane. ^{1}H NMR spectra of the powders show the only identifiable compounds in them to be the hydrazido complexes. However, there also are broad signals present in the dimethylamino and PR_3 regions, suggesting oligomeric decomposition products. Complexes **3b**,**d** could be partially purified in a similar manner, but these powders also contained substantial amounts of unidentifiable decomposition products. In no case could any of the complexes **3a–e** be completely purified.

The greater stability of the phosphine-substituted hydrazido complexes **3a–e** is most likely a result of both steric and electronic effects. In the case of $(CO)_5W{=}NNMe_2$, it was shown that the electron-donating dimethylamino substituent on the nitrene nitrogen greatly increased its stability relative to the arylnitrene $(CO)_5W{=}NPh$. The replacement of a CO on the metal center of **2** with a phosphine or phosphite would also be expected to increase the electron density at the nitrene nitrogen through improved backbonding. Evidence for the increased backbonding ability of the metal can be found in the lower IR stretching frequencies for the carbonyls in **3a–e** as compared to **2** (2069 and 1932 cm^{-1}).[3] Presumably, the same effect is present in the W=N bond, further strengthening the bonding of **3a–e**.[24]

The steric bulk of the phosphorus-containing ligands may, however, be the more significant factor in the increased stability of **3a–e** over **2**. The more sterically demanding ligands can help protect the metal and perhaps more importantly the nitrene nitrogen from attack by approaching species. In complexes **3a–e**, one would expect steric effects to force the dimethylamino group to preferentially orient itself away from the phosphine ligand. Such a configuration would point the lone pair of the nitrene nitrogen into the PR_3 ligand, providing it with more protection than would the relatively small carbonyls. Since $(CO)_5W{=}NNMe_2$ is known to be nucleophilic,[3] blocking the lone pair would presumably lead to kinetic stabilization.

Among the PR_3 ligands examined, the stabilities of **3a–e** increase as the cone angle of the ligand increases. This effect is illustrated by the fact that the PCy_3 complex **3c** can be isolated much more cleanly than the PMe_3 complex **3b**. The donor abilities of these phosphines are nearly identical,[25] suggesting that the

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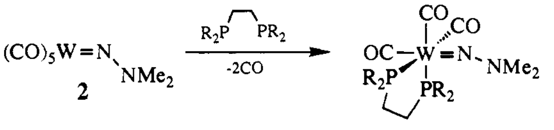
increased stability of **3c** results from the greater steric bulk of PCy_3. Where the electronic and steric effects seem to conflict, the steric effect appears to dominate. As mentioned earlier, complex **3e** can be isolated with much less decomposition than **3b**. This is despite the fact that $P(OPh)_3$ is a much better π-electron acceptor than PMe_3. Thus, the loss of electron density at the tungsten center appears to be more than offset by the increased steric bulk of the $P(OPh)_3$.

In the case of the (PMe_3)-substituted hydrazido complex **8a**, the extra phosphine ligand appears to destabilize the complex. Monitoring a reaction mixture of **3b** and **8a** by ^1H NMR shows that **8a** decomposes more quickly. This is counterintuitive based on both the steric and electronic arguments above. One possible explanation for this is found upon examination of a model of *mer*-$(CO)_3(PMe_3)_2W{=}NNMe_2$ (**8a**), which reveals that in order to avoid steric crowding between the PMe_3 ligands and the NMe_2 group the lone pair must be situated between the PMe_3 groups. This would thereby minimize the steric protection of the nitrene nitrogen in **8a**. A similar situation occurs with the labile **8b**.

Reaction of 2 with Bidentate Phosphines. The replacement of two carbonyl ligands of **2** by PMe_3 indicates that it is possible to exchange a second carbonyl ligand for a phosphine. Therefore, the chelating phosphines 1,2-bis(dimethylphosphino)ethane (DMPE) and 1,2-bis(diphenylphosphino)ethane (DPPE) were reacted with **2** in a fashion similar to that described above. Again, effervescence and darkening of the reaction solutions were observed, and the ^1H NMR spectra show new products which have been identified as *fac*-$(CO)_3(DMPE)W{=}NNMe_2$ (**10a**) and *fac*-$(CO)_3(DPPE)W{=}NNMe_2$ (**10b**), respectively (eq 4).



(4)

10a R=Me
10b R=Ph

The spectroscopic data for **10a,b** are summarized in Table II. Most notably, the ^{31}P NMR spectra show one signal, indicating both phosphorus atoms are equivalent and therefore cis to the hydrazido ligand. ^{13}C NMR shows two different CO signals in a 2:1 ratio, representing the carbonyls cis and trans to the hydrazido ligand. The *cis*-CO signal is split into a doublet of doublets due to coupling with the cis and trans phosphines, confirming the facial structure.

^{15}N NMR spectra of **10a,b** again show a downfield signal for N_α, indicating that the hydrazido ligand is bent. In the case of **10a**, this ^{15}N signal is split into a triplet by coupling to the two equivalent phosphines ($^2J_{P-N}$ = 8.0 Hz). The dynamic ^1H NMR spectra of **10b** again show that the dimethylamino signal can be resolved into two signals in a 1:1 ratio at low temperatures (ΔG^* = 8.8 kcal/mol). Interestingly, the two methyl peaks show a large difference in chemical shift (292 Hz), suggestive of a strong anisotropic interaction of one of the methyl groups with the phenyl rings of DPPE. The rotation of the dimethylamino group of **10a** could not be frozen out within the limits of our experiment.

The stability of complexes **10a,b** appears to be greatly increased with respect to their monodentate counterparts **3a** and **3b**. Addition of hexane to a solution of the DMPE complex **10a** results in the formation of a black precipitate. ^1H NMR spectra of this precipitate show it to be mainly **10a** with a small number of unidentified decomposition peaks. This contrasts with the large amount of decomposition observed in precipitation of the PMe_3 complex **3b**.

In the case of the more sterically bulky DPPE complex **10b**, the effect of two phosphine ligands on stability is even more pronounced. Addition of hexane to the solution of **10a** results in the precipitation of the pure complex *fac*-$(CO)_3(DPPE)W{=}NNMe_2$ as a dark yellow powder. The solid is stable for days at −40 °C and can be recrystallized from CH_2Cl_2/hexane to form dark yellow crystals.

Crystal Structure of 10b. Identification of **10b** as the bent hydrazido complex *fac*-$(CO)_3(DPPE)W{=}NNMe_2$ was confirmed by X-ray crystallography. The complex crystallizes in the $P2_1/n$ space group, with one disordered CH_2Cl_2 solvent molecule cocrystallized per **10b**. Disorder prevented refinement of the solvent. The ORTEP of **10b** and important bond lengths and angles are shown in Figure 1.

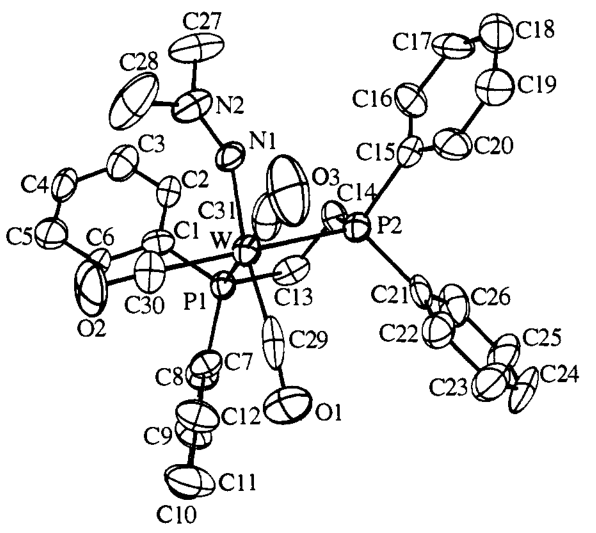


Figure 1. Molecular structure of **10b**. Thermal ellipsoids are drawn at the 40% probability level. Selected bond distances (Å) and angles (deg) are the following: W–C(29), 1.93 (2); W–C(30), 1.96 (2); W–C(31), 1.96 (2); W–N(1), 2.12 (1); W–P(1), 2.496 (4); W–P(2), 2.518 (4); N(1)–N(2), 1.21 (2); N(2)–C(27), 1.43 (2); N(2)–C(28), 1.45 (3); W–N(1)–N(2), 139 (1); N(1)–N(2)–C(27), 123 (2); N(1)–N(2)–C(28), 122 (2); N(1)–W–C(30), 100.1 (7); N(1)–W–C(29), 170.9 (7); P(1)–W–P(2), 79.3 (1).

The dimethylamino group of the complex is pointed directly away from the bulky DPPE ligand, thereby both minimizing the steric interaction and effectively blocking access to the N_α lone pair with the phenyl rings. Thus, kinetic stabilization of the reactive nitrene nitrogen by the bulky phosphorus ligands is consistent with the structure of the crystalline complex.

Prior to this report, there have been at least four other structurally characterized complexes containing a bent hydrazido ligand. Sutton has reported the structures of $[Cp_2WH(NHC_6H_4F)]PF_6$[26] and $CpRe(CO)_2[NN(CH_3)$-*p*-$C_6H_4OCH_3]$,[12] both containing strongly bent M–N–N skeletons (146.3° and 138.1°, respectively) and relatively long M–N bond distances (1.838 and 1.937 Å, respectively). $[ReOCl(PPh_3)_2(NNMePh)][PF_6]_2$,[27] recently prepared by Dilworth, has a similar bond angle (146.3°) and bond length (1.845 Å). Dilworth has also reported the strongly bent (M–N–N = 131.2°) $ReBr_2(NNPh)(PPh_3)_2(NNHPh)$,[28] but the bending in this complex is at least partially due to intramolecular hydrogen bonding between the hydrazido hydrogen and a bromide ligand.

Complex **10b** has pseudooctahedral geometry about the metal center, with normal W–P and W–C bond lengths. The geometry of the hydrazido ligand resembles that in the complexes described above, with a W–N–N bond angle of 139°. However, the W–N bond in this complex is exceptionally long, 2.12 Å, or over 0.28 Å longer than any previously reported linear (1.73–1.78 Å)[10c] or bent tungsten hydrazido complex. Interestingly, the pertinent bond lengths in **10b** most closely resemble those observed by Zubieta for the linear bis(hydrazido) complex $[Mo(NNMe_2)_2(MoS_4)_2][PPh_4]_2$ (**11**) (Mo–N = 2.13 Å, N–N = 1.16 Å).[29] The bonding in **11** was proposed to be best described by the resonance

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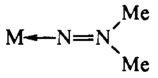
structure A in which the ligand is a coordinated 1,1-diazene.



A

The long W–N bond in **10b** is consistent with contribution of the zwitterionic resonance structure C to the bonding in this zero-valent hydrazido complex. This was previously hypothesized

B C

on the basis of the restricted rotation about the N–N bond and is further supported structurally by the short N–N bond (1.21 Å) and the near planarity of the amino nitrogen (deviating by 1.0°).

This type of resonance structure is very similar to that previously drawn for donor-stabilized Fischer carbenes, which also show a strong tendency toward a zwitterionic state with good donor substituents.[30] In fact, given that the atomic radius of carbon is slightly larger than that of nitrogen, tungsten–carbene bond lengths (2.15–2.21 Å)[30] are in good agreement with that observed for **10b**. This further supports the comparison of these zero-valent tungsten hydrazido complexes with their carbon analogues.

Conclusion

The replacement of the metal carbonyls in **2** with phosphines or phosphites illustrates the difference in reactivity between zero-valent hydrazido complexes and $(CO)_5W{=}NPh$, which has been shown previously to undergo nucleophilic attack at the nitrene nitrogen.[1b] This shift in reactivity is a result of the increased electron density at N_α in **2**, which should make that nitrogen less susceptible to nucleophiles. In this respect, Fischer carbenes and zero-valent nitrenes show parallel reactivity. However, hydrazido complex **2** diverges from heteroatom-stabilized carbenes in that carbonyl loss is much more facile. The increased lability of CO in $(CO)_5W{=}NNMe_2$ is most likely a result of the ability of these hydrazido complexes to donate the nitrogen lone pair to an electron-deficient five-coordinate intermediate.

It has been shown that replacing one or more CO's in **2** with phosphines or phosphites leads to a dramatic increase in the stability of these hydrazido complexes. Thus, one can prepare zero-valent nitrenes which vary from the transient $(CO)_5W{=}NPh$ to the crystalline *fac*-$(CO)_3(DPPE)W{=}NNMe_2$. The stability of these complexes appears to depend upon both the electron density at the nitrene nitrogen and steric protection of the reactive nitrene ligand. This has allowed the first structural characterization of a zero-valent hydrazido complex, *fac*-$(CO)_3(DPPE)W{=}NNMe_2$. The extremely long W=N double bond in **10b** and evidence for electron donation from the heteroatom substituent into the nitrene nitrogen support consideration of these complexes as nitrene analogues to Fischer carbenes. The spectroscopic similarities between **2** and **10b** suggest $(CO)_5W{=}NNMe_2$ also has a hydrazido ligand structurally quite similar to that described here.

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 3 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. Analytical gas chromatography (GC) was performed on an HP5890A chromatograph containing a 5 m × 0.25 mm column of SE-54 on fused silica. Elemental analyses were performed by Robertson Laboratories, Madison, NJ.

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.

Triphenylphosphin(dimethylamino)imine[31] **7** was prepared by literature methods. Pentacarbonyl[2,2-dimethylhydrazido]tungsten[3] **2** was prepared as reported previously and used in situ on the basis of a calculated yield of 65%.

Synthesis of *cis*-$(CO)_4PR_3W{=}NNMe_2$ (3a,c,e). The procedure for the preparation of **3a** is typical: To a 0.5 mL $CDCl_3$ (or CD_2Cl_2) solution of **2** (0.13 mmol) was added PPh_3 (35 mg, 0.13 mmol). The solution immediately darkened, and there was strong effervescence. ^1H NMR revealed the formation of **3a** in essentially quantitative yield. All spectral data of **3a–e** were obtained from the reaction mixtures unless otherwise noted, with these values tabulated in Table I.

Addition of 2 mL of hexane to the reaction mixtures of **3a–e** and storage at −40 °C for 12 h resulted in the precipitation of a black solid, which has been determined to contain the nitrene complex as well as varying amounts of unidentified decomposition material.

Synthesis of *cis*-$(CO)_4PR_3W{=}NNMe_2$ (3b,d). A typical procedure follows: To a 0.2-mL $CDCl_3$ solution of PMe_3 (5 mg, 0.66 mmol) cooled to −40 °C was added a −40 °C 0.5-mL $CDCl_3$ solution of complex **2** (0.65 mmol). The mixture was allowed to warm to room temperature, which led to a strong effervescence and darkening. ^1H NMR spectra showed the quantitative formation of **3b**.

Synthesis of *cis,mer*-$(CO)_3(PMe_3)_2W{=}NNMe_2$ (8a). To a 1-mL $CDCl_3$ solution of **2** (0.11 mmol) was added PMe_3 (20 mg, 0.26 mmol). The solution immediately darkened and effervesced. ^1H NMR spectra revealed the formation of **8a** in quantitative yield. When less than 2 equiv of PMe_3 were added, mixtures of **3b** and **8a** were generated. Monitoring this solution by ^1H NMR showed an accelerated disappearance of **8a** as compared to **3b**.

Synthesis of *cis,mer*-$(CO)_3[P(OMe)_3]_2W{=}NNMe_2$ (8b). To a 1-mL $CDCl_3$ solution of **2** (0.08 mmol) was added $P(OMe)_3$ (26 mg, 0.21 mmol). ^1H NMR spectra showed the formation of **8b** (ca. 35% yield), as well as the monosubstituted complex **3d** (ca. 20% yield) and substantial decomposition.

Synthesis of *fac*-$(CO)_3(DMPE)W{=}NNMe_2$ (10a). To a $CDCl_3$ solution of **2** (0.066 mmol) was added 1,2-bis(dimethylphosphino)ethane (11 mg, 0.073 mmol). ^1H NMR spectra showed the formation of **10a** in quantitative yield. Addition of 2 mL of hexane to the reaction mixture and storage at −40 °C for 12 h resulted in the precipitation of a black powder. Similar to **3a,c,e**, this contained **10a** as well as decomposition products. Recrystallization from CH_2Cl_2/hexane did not improve the purity of **10a** and produced more decomposition products.

Synthesis of *fac*-$(CO)_3(DPPE)W{=}NNMe_2$ (10b). To a 3-mL $CDCl_3$ solution of **2** (0.28 mmol) was added 1,2-bis(diphenylphosphino)ethane (110 mg, 0.28 mmol). ^1H NMR spectra of the reaction solution showed the quantitative formation of **10b**. Addition of 6 mL of hexane to this solution and storage at −40 °C for 12 h resulted in the precipitation of a black powder of **10b** contaminated with $W(CO)_6$ (a byproduct of the formation of **2**). Recrystallization of **10b** from CH_2Cl_2/hexane gave dark yellow crystals of **10b**·CH_2Cl_2 (120 mg, 59% yield). Anal. Calcd for $C_{32}H_{32}Cl_2N_2O_3P_2W$: C, 47.49; H, 3.99; N, 3.46; Cl, 8.76. Found: C, 47.39; H, 3.78; N, 3.49; Cl, 8.21.

Crystal Structure of 10b. X-ray data collection was performed on a crystal enclosed in a 0.5-mm capillary under N_2. The diffractometer was a Syntex $P2_1$ equipped with Mo radiation. Data reduction and refinement were done on a DEC microVAX computer using SDP software. Observed data were corrected for decay and Lorentz and polarization factors. A ψ-scan absorption correction was collected but not applied, because the amount of correction was small (<4%). The structure was solved by using the Patterson heavy-atom method and refined by full-matrix least squares. Non-hydrogen atoms were refined anisotropically, except for the chlorine atoms in the CH_2Cl_2 solvent, which were highly disordered. Hydrogens were refined in idealized positions with the C–H distance fixed at 0.95 Å. U_{iso}s for the hydrogen atoms were fixed at $1.2U_{iso}$ of the attached carbon atom.

Crystal Data for 10b. Empirical formula, $C_{31}H_{30}O_3N_2P_2W$ (CH_2Cl_2); color, habit, yellow plates; crystal size, 0.20 × 0.30 × 0.25 mm^3; crystal system, monoclinic; space group, $P2_1/n$; $a = 8.4406\ (20)$ Å, $b = 23.9747\ (60)$ Å, $c = 16.5073\ (40)$ Å; $\beta = 92.36\ (2)°$; $V = 3337.6\ (25)$ Å^3; $Z =$

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4; fw = 724.39; D_{calc} = 1.611; abs coeff = 38.243; diffractometer, Syntex $P2_1$; radiation, graphite monochromated Mo $K\alpha$ (0.71073 Å); 2θ range = 3–45°; scan type, θ–2θ; scan speed, var. 4–29; standard reflections, 3 standard/100 reflections; reflections collected = 4855; independent reflections = 4684; observed reflections ($F_o > 3\sigma(F_o)$) = 3025; data/parameter = 7.77; final $R(F)$, $R(wF)$ = 6.3%, 7.2%; weighting scheme, $1/w = \sigma^2(I)/4F^2 + 0.000225F^2$; final GOF = 4.408; Δ/σ (mean) = 0.02; highest peak in difference map = 2.18 e/Å^3 (all peaks larger than 0.807 e/Å^3 were tungsten ghosts).

Synthesis of $(CO)_5W(Ph_3P{=}NNMe_2)$ (6). To the oil $(CO)_5W(THF)$ (150 mg, 0.42 mmol) was added $Ph_3P{=}NNMe_2$ (**7**) (100 mg, 0.31 mmol) dissolved in 1 mL of $CDCl_3$. This resulted in the quantitative conversion of **7** to **6**. Spectral data for **6** were obtained on this solution. **6**: ^1H NMR ($CDCl_3$) δ 2.53 (s, 6 H), 7.2–7.8 (m, 15 H). ^{13}C NMR ($CDCl_3$) δ 202.06 (CO_{trans}), 199.21 (CO_{cis}), 49.12 (CH_3). ^{31}P NMR ($CDCl_3$) δ 32.69 (s). **7**: ^1H NMR ($CDCl_3$) δ 2.33 (s, 6 H), 7.4–7.7 (m, 15 H). ^{13}C NMR δ 51.63 (d, $^3J_{P-C}$ = 10.0 Hz, CH_3). ^{31}P NMR ($CDCl_3$) δ 18.60 (s, broad).

Kinetics of Reaction of 2 with PPh_3 and $P(OPh)_3$. To three separate NMR tubes containing a 0.5-mL $CDCl_3$ solution of **2** (0.010 mmol) and cooled to −50 °C were added 1.1 equiv of PPh_3 (3 mg, 0.011 mmol), 3.1 equiv of PPh_3 (8 mg, 0.031 mmol), and 6.0 equiv of PPh_3 (16 mg, 0.060 mmol). The solutions were warmed to −20 °C in the NMR probe, and the disappearance of **2** was monitored every 5 min for 1 h. Similarly, the disappearance of **2** with 1.6 equiv of $P(OPh)_3$ (5 mg, 0.016 mmol) was monitored. The plot of ln [**2**] vs time gave a straight line with a slope equal to k_{obs}. Error in k_{obs} was based upon 5% NMR integration error.

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Supplementary Material Available: Tables of bond distances and angles, hydrogen atom coordinates, and thermal parameters (13 pages); table of observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

A σ-Bond Metathesis Mechanism for Dehydropolymerization of Silanes to Polysilanes by d^0 Metal Catalysts

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Abstract: A mechanism for the dehydropolymerization of hydrosilanes to polysilanes, as catalyzed by early-transition-metal metallocene derivatives, is proposed. This mechanism is based on two σ-bond metathesis reactions that pass through four-center transition states: (1) the dehydrometalation of silane, $H(SiHR)_nH$, with a metal hydride to give hydrogen and a silyl derivative, $M(SiHR)_nH$, and (2) coupling of the metal silyl derivative with more hydrosilane, $H(SiHR)_mH$, to produce $H(SiHR)_n(SiHR)_mH$ and regenerate the active metal hydride catalyst. This proposal is based on a number of observed, stoichiometric σ-bond metathesis reactions involving zirconocene and hafnocene complexes. These reactions, which involve silicon, hydrogen, and a d^0 metal center, are rather facile and apparently reflect the tendency of silicon to expand its coordination sphere under these conditions. One reaction of this type is rapid MH/SiH hydrogen exchange, for example between $PhSiH_3$ and $CpCp^*MHCl$ (**1**, M = Zr, or **2**, M = Hf), which is observed via deuterium labeling. Hydrogenolysis of $CpCp^*M[Si(SiMe_3)_3]Cl$ (**3**, M = Zr, and **4**, M = Hf) provides a convenient route to the monomeric hydride complexes **1** and **2**, respectively. The first step in the proposed polymerization mechanism, which is the reverse of M–Si bond hydrogenolysis, is observed in stoichiometric reactions of **1** or **2** with $PhSiH_3$ to give hydrogen and the phenylsilyl complexes $CpCp^*M(SiH_2Ph)Cl$ (**5**, M = Zr, and **6**, M = Hf). The thermolytic decomposition of **6** to **2** results in Si–Si bond formation, with the production of polysilane oligomers. This second-order reaction exhibits a deuterium isotope effect at 75 °C of 2.9 (2) and activation parameters ($\Delta H^{\ddagger}$ = 19.5 (2) kcal mol^{-1} and $\Delta S^{\ddagger}$ = −21 (6) eu) that suggest a four-center transition state. The second-order reaction of **6** with $PhSiH_3$ (to give **2** and $(SiHPh)_n$ polysilanes) was also studied kinetically and found to exhibit similar kinetic parameters. This σ-bond metathesis reaction, which corresponds to the second step in the proposed mechanism, is believed to pass through a four-center transition state that results from interaction of the $CpCp^*(Cl)Hf{-}SiH_2Ph$ and $H{-}SiH_2Ph$ bonds. Evidence for the role of hydride complexes as true catalysts is obtained by comparing gel permeation chromatograms for polysilanes obtained from both **3** and **1** as catalysts. Observed reactions of $CpCp^*Hf[Si(SiMe_3)_3]Me$ (**7**) with $PhSiH_3$, to give $CpCp^*Hf(SiH_2Ph)Me$ (**8**) and then $CpCp^*Hf(H)Me$ (**9**), model proposed processes for the activation of catalyst precursors. The step-growth character of the reaction is illustrated by the slow dehydrocoupling of $PhSiH_3$ by $Cp^*_2HfH_2$, which allows observation of early polysilane intermediates (di-, tri-, and tetrasilane). The participation of $M(SiHPh)_nH$ complexes as intermediates in dehydrocoupling was investigated. Partly on the basis of the observed reaction of $CpCp^*Hf[(SiHPh)_3H]Cl$ (**11**) with $PhSiH_3$ to give **6** and $H(SiHPh)_3H$, it is concluded that a preferred dehydrocoupling pathway involves monosilyl intermediates, $MSiH_2Ph$, and chain growth by one monomer unit per catalytic cycle. Implications of the proposed mechanism are discussed.

Current interest in polysilane polymers results from their unusual electronic, optical, and chemical properties and the potential applications derived therefrom.[1] The most convenient route to these polymers, the Wurtz coupling of dichlorosilanes by alkali metals, is severely limited as a general method since it tends to produce only moderate yields and does not tolerate many functional groups.[1] Because substituent effects can significantly influence the chemical and physical properties of these polymers,[1] new synthetic routes which allow more control over the polymer structure are desired. Alternative polymerization methods that have been developed include chloride-catalyzed redistribution of methylchlorodisilanes,[2] electrochemical synthesis,[3] polymerization

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