Organometallics 1991, *10*, 541-543

The bimetallic compound 8 is also stable in strongly coordinating solvents such as CH_3CN or THF but does react with water and protonic solvents.

Parallel to the chemistry demonstrated for the phosphoranimines, an alternate route to the new arsenic-based Ti(IV)-Pd(II) bimetallic 8 was provided by the reaction of the Pd(II) complex 6, readily formed from 2 and $PdCl_2(PhCN)_2$, with $CpTiCl_3$ (Scheme II).

The new methodology for formation of early-late-transition-metal bimetallics (Schemes I and II) promises to provide a versatile route, because the precursors of types 5 and 6 are readily accessible for a variety of late (such as Rh(I), Ir(I), or Pd(II)) metals and compounds such as 3 and 4 are readily synthesized for early (such as W(VI), Zr(IV), V(V)) transition metals.[10] Further applications of the sequences described herein are presently under investigation.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

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(13) (a) The reaction of $PdCl_2(PhCN)_2$ with 4 to obtain 8 was carried out under experimental conditions similar to those described above for the preparation of 7[11] (yield of 8 90%; mp 190 °C dec). Anal. Calcd for $C_{31}H_{29}Cl_4NAsPPdTi$: C, 41.83; H, 3.26; N, 1.57; Cl, 15.94. Found: C, 41.78; H, 3.28; N, 1.55; Cl, 15.92. ^1H NMR ($CDCl_3$): phenyl rings δ 7.40, 7.67, 7.87 (m, 20 H); $AsCH_2CH_2P$ δ 2.60 (m, 2 H), 3.20 (m, 2 H); cyclopentadienyl ring δ 6.65 (s, 5 H). (b) The reaction of $CpTiCl_3$ with 6 (prepared as described in ref 8) was carried out under experimental conditions similar to those described above for the transformation of 5 to 7 (yield 85%). The physical constants, analytical data, and spectroscopic data for 8 prepared via this route were identical with those listed above.

Direct Observation of the Low-Valent Hydrazido Complex $(CO)_5W{=}NNMe_2$, a Nitrene Analogue of the Heteroatom-Stabilized Fischer Carbenes

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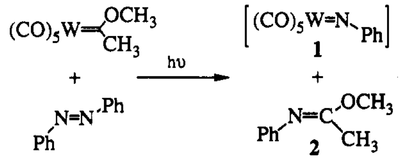
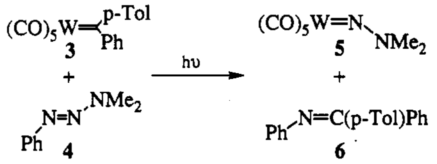
Received December 18, 1990

Summary: The low-valent hydrazido (or heteroatom-stabilized nitrene) complex $(CO)_5W{=}NNMe_2$ (**5**) was synthesized via photochemical metathesis of the triazene $PhN{=}NNMe_2$ (**4**) with $(CO)_5W{=}C(p\text{-Tol})Ph$ (**3**). Assignment of **5** as a bent terminal hydrazido complex was made on the basis of its multinuclear NMR and IR spectra.

We recently reported the generation of the low-valent tungsten nitrene $(CO)_5W{=}NPh$ (1) by reaction of $(CO)_5W{=}C(OMe)Me$ with photochemically generated *cis*-azobenzene (eq 1). Complex 1 was not directly observed but, rather, was identified by its trapping and decomposition products.[1,2] Although 1 and its chromium congener have been invoked as intermediates in the reactions of Fischer carbenes with azo compounds and nitroso compounds,[3] these species have not yet been directly observed. We now report the generation and direct observation of the low-valent hydrazido (or heteroatom-stabilized nitrene) complex $(CO)_5W{=}NNMe_2$ (5) from the photochemical metathesis between $(CO)_5W{=}C(p\text{-Tol})Ph$ (3) and the triazene $PhN{=}NNMe_2$ (4) (eq 2). Although 5 could not be isolated, it is persistent for several hours in solution at room temperature and has been characterized through IR and multinuclear NMR spectroscopy.



(1)



(2)

Metal hydrazido complexes are common in the literature, but the reported examples are almost exclusively confined to high-valent metals with two or less d electrons.[4] In general, the lack of electron density around the metal causes the hydrazido ligands to adopt the linear (or nearly linear) geometry required for donation of 4e, so that strongly bent terminal hydrazido complexes have remained extremely rare.[5] The low-valent hydrazido complex 5 is electronically quite different, in that 4e donation would result in a 20e complex and bending of the hydrazido ligand is expected.[6] Given that 5 and the related nitrene (or imido) complex 1 are isoelectronic with Fischer carbenes, insight into their properties is perhaps better gained by comparing 5 and 1 to the carbene complexes.

Fischer carbenes of the type $(CO)_5M{=}CRR'$ (R, R' = H, alkyl, aryl) are highly reactive, highly electrophilic species, while their heteroatom-substituted counterparts

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

(2) Sleiman, H. F.; Mercer, S.; McElwee-White, L. *J. Am. Chem. Soc.* **1989**, *111*, 8007-8009.

(3) (a) Hegedus, L. S.; Kramer, A. *Organometallics* **1984**, *3*, 1263-1267. (b) Pilato, R. S.; Williams, G. D.; Geoffroy, G. L.; Rheingold, A. L. *Inorg. Chem.* **1988**, *27*, 3665-3668. (c) Herndon, J. W.; McMullen, L. A. *J. Organomet. Chem.* **1989**, *368*, 83-101.

(4) Recent reviews on hydrazido complexes include (a) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley-Interscience: New York, 1988. (b) Hidai, M. In *Molybdenum Enzymes*; Wiley-Interscience: New York, 1985; pp 285-341. (c) Chatt, J.; da Camara Pina, L. M.; Richards, R. L., Eds. *New Trends in the Chemistry of Nitrogen Fixation*; Academic Press: London, 1980.

(5) For examples of structurally characterized bent hydrazido complexes see: (a) Barrientos-Penna, C. F.; Einstein, F. W. B.; Jones, T.; Sutton, D. *Inorg. Chem.* **1982**, *21*, 2578-2585. (b) Einstein, F. W. B.; Jones, T.; Hanlan, A. J. L.; Sutton, D. *Inorg. Chem.* **1982**, *21*, 2585-2589.

(6) Arndtsen, B. A.; Sleiman, H. F.; Chang, A. K.; McElwee-White, L. Submitted for publication.

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Table I. ^{15}N NMR Shift Ranges for N_α in Metal Complexes[a]

linkage	δ(linear)	δ(bent)
M-NO	-80 to +80	350–800
N-NNR	-55 to -25	298–327
$M-NNR_2$	-98 to -58	420.1[b]

[a] Positive shifts are downfield of CH_3NO_2 at 0.0 ppm. [b] For **5**.

$(CO)_5M{=}CXR$ (X = OR, SR, NR_2) are stabilized significantly through the donation of π electron density into the empty p orbital of the carbene carbon.[7] The rapid addition of PPh_3 to the nitrene nitrogen in $(CO)_5W{=}NPh$[2] indicates similar electrophilicity in the nitrene complexes $(CO)_5W{=}NR$. Therefore, heteroatom substituents on the nitrene nitrogen in complexes such as $(CO)_5W{=}NX$ (X = OR, SR, NR_2) could be expected to render these complexes less reactive.

Photolysis (medium-pressure Hg arc, Pyrex filtered) of a 2:1 mixture of triazene **4** and carbene **3** in $CDCl_3$ at -40 °C for 40 min resulted in a 94% ^1H NMR yield of imine **6**[10] and another product which gave rise to one ^1H NMR singlet at δ 3.83. Assigning this singlet to a NMe_2 group allows a 68% NMR yield (based on **3**) to be calculated for the point at which carbene **3** is consumed. This product is highly vulnerable to secondary photolysis, and continued irradiation resulted in decreased yields. When it sat at room temperature in the dark for 1 day, the compound decomposed, leading to a complex mixture of unidentified species. On the basis of the experiments described below, the signal at δ 3.83 was ascribed to $(CO)_5W{=}NNMe_2$ (**5**).[11]

Assignment of a $(CO)_5W$ fragment to **5** was made upon the observation of a typical pentacarbonyl pattern in the carbonyl region (ν_{W-CO} ($CHCl_3$): 1932 (vs), 2069 (m) cm^{-1}) of its IR spectrum. Additional evidence came from the ^{13}C NMR spectrum of the isotopically labeled compound $(^*CO)_5W{=}NNMe_2$ (**5**-[^{13}C]; the asterisk indicates 16% ^{13}C label), prepared by photolysis of $(^*CO)_5W{=}^*C(p\text{-Tol})Ph$[12] (**3**-[$^{13}C$]) with **4**. The ^{13}C NMR spectrum of **5**-[^{13}C] showed two peaks in the tungsten carbonyl region at δ 197.4 and 213.2 in an approximately 4:1 ratio, which were assigned to the cis and trans CO's of the $(CO)_5W$ moiety. The only other ^{13}C-enriched signals found in the spectra were those corresponding to free CO (δ 184.2), $W(CO)_6$ (δ 191.1), and the two isomers of $PhN{=}C(p\text{-Tol})Ph$ at δ 168.2 and 169.2, ruling out the presence of the $C(p\text{-Tol})Ph$ fragment or any other carbonyl-containing fragment[15] in **5**.

Further studies were carried out on the ^{15}N-enriched (99%) complexes $(CO)_5W{=}^{15}NNMe_2$ (**5**-[^{15}N]) and $(CO)_5W{=}^{15}N^{15}NMe_2$ (**5**-[$^{15}N]_2$), which were synthesized by photolysis of carbene **3** with $PhN{=}^{15}NNMe_2$ (**4**-[^{15}N])and $PhN{=}^{15}N^{15}NMe_2$ (**4**-[$^{15}N]_2$), respectively.[16] In the ^1H NMR spectra of **5**-[^{15}N] and **5**-[$^{15}N]_2$, the methyl signals appeared as a doublet ($^3J_{NH}$ = 1.8 Hz) and an unresolved doublet of doublets ($^2J_{NH}$ = 2.2 Hz), respectively. The ^{15}N NMR spectrum of complex **5**-[^{15}N] showed a singlet at δ 420.1, while that of **5**-[$^{15}N]_2$ contained doublets at δ 420.1 and -79.0 ($^1J_{NN}$ = 13.2 Hz).[17] The magnitude of $^1J_{NN}$ suggests partial N-N double-bond character,[18a,b] a feature supported by the variable-temperature ^1H NMR results (vide infra).

Scheme I

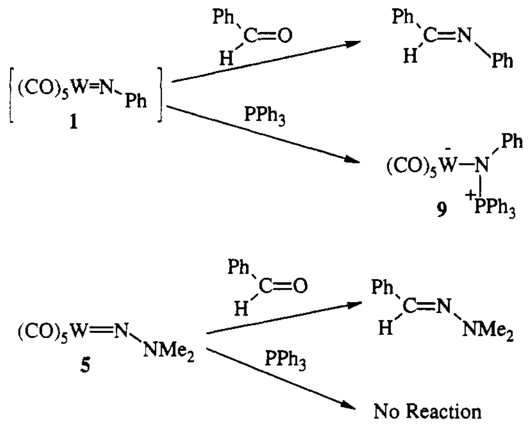

Table I shows a comparison of the ^{15}N data of **5** with the chemical shifts of linear hydrazido ligands,[18,19] as well as linear and bent nitrosyl[18c] and diazenido[20] ($MN_\alpha{=}N_\beta R$) complexes. Both nitrosyl and diazenido complexes exhibit an extreme downfield shift for N_α upon bending. The chemical shift for N_α in complex **5** is at least 350 ppm downfield of the reported N_α resonances of linear hydrazido complexes. This constitutes strong evidence for bending in the hydrazido ligand of **5**.

The assignment of a bent terminal $NNMe_2$ ligand in **5** is supported by its NMR behavior at low temperatures. At room temperature, the ^1H NMR spectrum for **5** in CD_2Cl_2 shows a sharp singlet at δ 3.88. At low temperature, this signal broadens and eventually emerges as two distinct signals of equal intensity, appearing at δ 3.79 and 3.90 at -100 °C. The ^{13}C NMR spectrum of **5** at -100 °C retains its single pentacarbonyl fragment pattern, while the methyl carbons split into two signals at δ 64.92 and 59.41.

The variable-temperature NMR spectra of complex **5** were interpretable in terms of a hindered rotation about the N-N bond of the bent hydrazido ligand. Any structure with a linear hydrazido ligand is excluded, as the methyl groups would remain equivalent. Similarly, the single pentacarbonyl fragment in the ^{13}C NMR spectrum at low temperatures eliminates the possibility of a hydrazido ligand bridging unsymmetrically between two $(CO)_5W$ moieties, as does the high yield of **5** (68%). The coales-

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(7) For example, the complex $(CO)_5W{=}CHPh$ decomposes at temperatures above -56 °C[8] while $(CO)_5W{=}C(OMe)Ph$ is indefinitely stable at room temperature.[9]

(8) Casey, C. P.; Polichnowski, S. W.; Shusterman, A. J.; Jones, C. R. *J. Am. Chem. Soc.* **1979**, *101*, 7282–7292.

(9) Fischer, E. O.; Massböl, A. *Angew. Chem., Int. Ed. Engl.* **1964**, *2*, 580–581.

(10) Similar results are obtained in other solvents such as CD_2Cl_2 and toluene-d_8, ruling out the involvement of $CDCl_3$ in the photochemistry.

(11) Control experiments with authentic materials demonstrated that this signal was not due to the potential products Me_2NNH_2, $Me_2NN{=}NNMe_2$, or their $W(CO)_5$ complexes, nor was it due to $(CO)_5W(PhN{=}NNMe_2)$.

(12) Conversion of $(^{13}CO)W(CO)_5$[1] to the carbene $(^*CO)_5W{=}^*C(OMe)Ph$ (**7**-[^{13}C]) by the method of Fischer[13] and reaction of **7**-[^{13}C] with PhLi and then HCl[14] afforded $(^*CO)_5W{=}^*C(p\text{-tol})Ph$ (the asterisk denotes 16% label at the indicated positions).

(13) Fischer, E. O.; Schubert, U.; Kleine, W.; Fischer, H. *Inorg. Synth.* **1979**, *19*, 164–167.

(14) Casey, C. P.; Burkhardt, T. J.; Neumann, S. M.; Scheck, D. M.; Tuinstra, H. E. *Inorg. Synth.* **1979**, *19*, 180–183.

(15) For example, isocyanate complexes have been obtained in other reactions postulated to produce transient low-valent nitrene complexes: (a) Collman, J. P.; Kubota, M.; Vastine, F. D.; Sun, J. Y.; Kang, J. W. *J. Am. Chem. Soc.* **1968**, *90*, 5430–5437. (b) Collman, J. P.; Hoffman, N. W.; Hosking, J. W. *Inorg. Synth.* **1970**, *12*, 8–11.

(16) **4**-[^{15}N] was synthesized by coupling of dimethylamine with the diazonium salt $[PhN{\equiv}^{15}N]^+$, prepared by diazotization of aniline with $Na^{15}NO_2$. For **4**-[$^{15}N]_2$, the dimethylamine was also ^{15}N-labeled.

(17) ^{15}N NMR spectra are referenced to CH_3NO_2 at 0 ppm, with downfield shifts positive.

(18) (a) Mason, J. In *Multinuclear NMR*; Mason, J., Ed.; Plenum Press: New York, 1987. (b) Witanowski, M.; Stefaniak, L.; Webb, G. A. *Annu. Rep. NMR Spectrosc.* **1986**, *18*, 593–596. (c) von Philipsborn, W.; Muller, R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 383–413. (d) Mason, J. *Chem. Rev.* **1981**, *81*, 205–227.

(19) Donovan-Mtunzi, S.; Richards, R. L.; Mason, J. *J. Chem. Soc., Dalton Trans.* **1984**, 1329–1332.

(20) Dilworth, J. R.; Kan, C. T.; Richards, R. L.; Mason, J.; Stenhouse, I. A. *J. Organomet. Chem.* **1980**, *201*, C24–C26.

cence temperature for **5** was estimated to be −84 °C, which gives a rough estimate of the barrier for N–N rotation of $\Delta G^{\ddagger} \simeq 9.2$ kcal/mol.[21,22] A similar phenomenon has been observed in the chemistry of the amino-substituted Fischer carbenes $(CO)_5W{=}C(NR_2)R'$, where the barrier for rotation of the C–N bond is high enough that two isomers are observed at room temperature ($\Delta G^{\ddagger} > 25$ kcal/mol).[22a]

Preliminary experiments on the reactivity of **5** provide a comparison with the behavior of the non-heteroatom-stabilized complex $(CO)_5W{=}NPh$. The reaction of $(CO)_5W{=}NPh$ with aldehydes has been found to yield phenylimines (Scheme I).[6] Likewise, when an excess of benzaldehyde was added to the reaction mixture after formation of **5** and the mixture was left at room temperature in the dark for 12 h, the hydrazone $Me_2NN{=}CHPh$[23] was formed in 85% yield (based on initial **5**) by ^1H NMR spectroscopy.

Although $(CO)_5W{=}NPh$ (**1**) reacts rapidly with PPh_3 to produce the phosphine ylide **9** (Scheme I),[2] $(CO)_5W{=}NNMe_2$ did not react with PPh_3 at room temperature. The lack of reactivity of **5** toward PPh_3 as compared to that of **1** implies a reduced electrophilicity at the nitrene nitrogen. This situation has a parallel in the chemistry of Fischer carbenes: while PPh_3 readily reacts (−78 °C) with the highly electrophilic $(CO)_5W{=}CHPh$ to give a phosphine ylide,[8] heteroatom-stabilized Fischer carbenes such as $(CO)_5W{=}C(OMe)Me$ do not form ylides with PPh_3 even at room temperature.[24]

In conclusion, we have prepared the low-valent hydrazido (or heteroatom-stabilized nitrene) complex $(CO)_5W{=}NNMe_2$ (**5**) by photochemical metathesis of $(CO)_5W{=}C(p\text{-Tol})Ph$ with the triazene $PhN{=}NNMe_2$. Spectroscopic evidence is consistent with a bent terminal hydrazido ligand in **5**. As in the Fischer carbenes, the heteroatom-containing substituent results in increased stability and decreased electrophilicity of **5** as compared to $(CO)_5W{=}NPh$.

Acknowledgment. This work was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the NSF-MRL Program through the Center for Materials Research at Stanford University.

Supplementary Material Available: Experimental procedures for the generation of $(CO)_5W{=}NNMe_2$ and trapping with benzaldehyde, ^1H NMR spectra of **5**, **5**-[^{15}N], and **5**-[^{15}N]$_2$, ^{15}N NMR spectra of **5**-[^{15}N] and **5**-[^{15}N]$_2$, the ^{13}C NMR spectrum of **5**-[^{13}C] and the IR spectrum of **5** (9 pages). Ordering information is given on any current masthead page.

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(21) The rate constant for the exchange was calculated to be 104.04 s^{-1} by using $k = (\pi)\Delta\nu/2^{1/2}$.

(22) (a) Kreiter, C. G.; Fischer, E. O. *Proceedings of the XXXIII International Congress of Pure and Applied Chemistry*; Butterworths: London, 1971; Vol. 6, pp 151–168. (b) Fischer, E. O.; Kreiter, C. G.; Kollmeier, H. J.; Muller, J.; Fischer, R. D. *J. Organomet. Chem.* **1971**, *28*, 237–258. (c) Kegley, S. E.; Brookhart, M.; Husk, G. R. *Organometallics* **1982**, *1*, 760–762.

(23) Authentic $Me_2NN{=}CHPh$ was synthesized by combining 1,1-dimethylhydrazine with benzaldehyde in toluene-d_8 at room temperature in the presence of 4-Å molecular sieves.

(24) Kreissl, F. R.; Fischer, E. O.; Kreiter, C. G.; Fischer, H. *Chem. Ber.* **1973**, *106*, 1262–1276.

Computational Evidence for a Nonplanar η^3-Cyclopentadienyl Ligand in Dicarbonylbis(cyclopentadienyl)chromium and the Pathway for the $\eta^5 \leftrightarrow \eta^3$ Ring Interchange

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Summary: The geometry of $(Cp)_2Cr(CO)_2$ (Cp = cyclopentadienyl) was completely optimized with the use of the partial retention of diatomic differential overlap (PRDDO) method and found to contain an η^5-Cp and a nonplanar η^3-Cp ring. The pathway for the interconversion of the two bonding modes was also calculated and shown to be facile via a $(\eta^3\text{-Cp})_2Cr(CO)_2$ complex in which both Cp rings are planar.

There are many ways in which a cyclopentadienyl (Cp) ligand is capable of bonding to a metal atom.[1] A systematic molecular orbital study of some of the various binding modes has recently been published.[2] In almost every case, the cyclopentadienyl ring is planar; however, nonplanar Cp coordination has been observed in a few organometallic systems. The first definitive proof of a nonplanar Cp ring was provided when the X-ray crystal structure of $(Cp)_2W(CO)_2$ revealed an η^3-Cp ring in which two carbon atoms were bent out of the plane of the other three by an angle of 20°.[3] A similar η^3-bonding mode has been suggested[4] for $(Cp)_2Cr(CO)_2$ on the basis of infrared spectral data, but this structure has not been confirmed by X-ray crystallography. More recently it has been shown that the Cp ligands in $(Cp)_2Cr(CO)_2$ are not bound to the metal in the same manner and that the interchange of bonding modes occurs with an activation energy of 13.5 kcal/mol.[5] While the authors imply an η^3-Cp ligand, in reality any bonding mode that is not the same for both ligands could account for the observed NMR spectra. In this communication, we present the first molecular orbital study in which an *optimized* geometry for a nonplanar η^3-Cp ligand is calculated and shown to represent the minimum energy conformation on the potential energy surface. We also present a simple rationale for the bent

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(1) For example, in a review article (O'Connor, J. M.; Casey, C. P. *Chem. Rev.* **1987**, 87, 307) the authors compiled 10 different Cp binding modes. Early theoretical studies of olefin distortion upon binding to metals include: Albright, T. A.; Hoffmann, R.; Hofmann, P. *Chem. Ber.* **1978**, *111*, 1591. Hoffmann, R.; Hofmann, P. *J. Am. Chem. Soc.* **1976**, *98*, 598.

(2) Hansen, L. M.; Marynick, D. S. *Organometallics* **1989**, *8*, 2173.

(3) Huttner, G.; Brintzinger, H. H.; Bell, L. G.; Friedrich, P.; Bejenke, V.; Neugebauer, D. *J. Organomet. Chem.* **1978**, *145*, 329.

(4) van Raaij, E. U.; Brintzinger, H. H. *J. Organomet. Chem.* **1988**, *356*, 315.

(5) Millar, J. M.; Kastrup, R. V.; Harris, S.; Horvath, I. T. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 194.

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