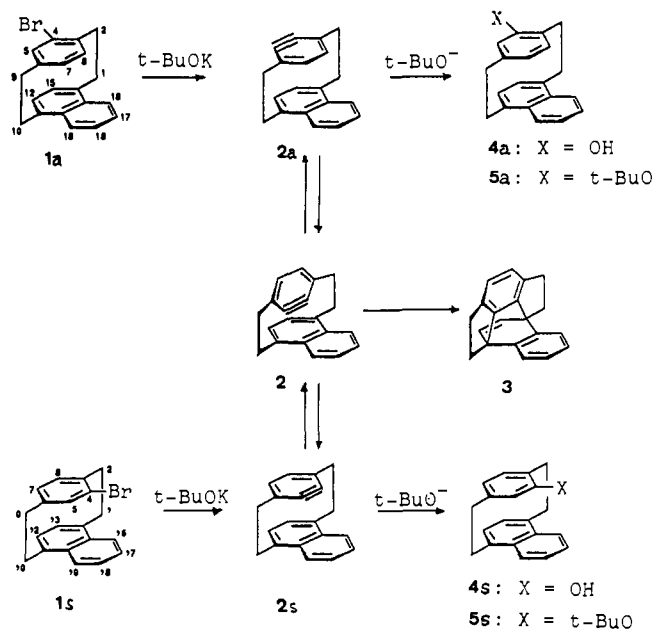


Table I. Reaction of *anti*- and *syn*-4-Bromo[2.2](1,4)naphthalenoparacyclophanes with Potassium *tert*-Butoxide

substrate	isolated yields (%)				
	3	4a	5a	4s	5s
1a	7.7	21.0	20.2	15.3	a
1s	2.6 ^b	16.6	a	27.8	8.2 ^b

^a A minor amount of the compound was formed, as confirmed on silica gel TLC. ^b 3 and 5s were obtained as a mixture, and the yields were determined by ¹H NMR spectroscopy.

Scheme I



In the reaction of 1a, 2a is first generated. Only a portion of 2a traps butoxide anion to give 4a and 5a, and the remainder is converted into 2s by way of dehydrocyclophane 2, whose aryne ring is arranged perpendicularly to the facing ring. This 2 can itself undergo internal cycloaddition to give 3. The resulting 2s undergoes similar butoxide anion trapping to give 4s and 5a and also conversion into 2a. This interconversion of 2a and 2s (or aryne-ring rotation, $2a \rightleftharpoons 2 \rightleftharpoons 2s$) continues without reaction until all dehydrocyclophane molecules are consumed. As a result, 4a and 5a are formed in preference to the other products. In clarifying the reaction mechanism, it is also important to know whether retro Diels-Alder reaction of 3 reverting to 2 takes place. Considering the large bond-angle distortion observed around the bridgehead,⁵ one may suppose the reaction to occur. However, 3 did not give any external adducts under the same reaction conditions as described above, indicating that 3 did not revert to 2.

The reaction of 1s proceeds via the reverse aryne route starting from 2s, leading to the preferred formation of 4s and 5s.

Previous work by Longone et al. demonstrated that 5,6-dehydro[3.3]paracyclophane, generated from 5-bromo[3.3]-paracyclophane and a large excess of potassium *tert*-butoxide, gives an internal cycloadduct similar to 3 but does not give adducts arising from *tert*-butoxide addition to the dehydrocyclophane.¹ This is in sharp contrast to similarly generated 4,5-dehydro[2.2]paracyclophane, where such external adducts dominate.^{2,3} Dehydrocyclophanes 2a and 2s give not only external adducts but also an internal one, probably by way of aryne-ring rotation. This suggests that the aryne ring in 2a and 2s has a sufficiently long lifetime to rotate without reaction occurring at a temperature of 180 °C, despite the 20-fold excess of base used.

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Simple Low-Valent Amido, Imido, and Nitrido Complexes of Tungsten

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Most transition metal imido (or nitrene) complexes are nucleophilic at nitrogen,¹ but certain species exhibit reactivity patterns indicative of electrophilic character.²⁻⁵ For example, high-valent manganese(V)^{2a} and iron(V)^{2b} derivatives, activated by trifluoroacetyl and tosyl groups, respectively, transfer the nitrene unit to alkenes to produce aziridines. McElwee-White et al. have reported that the putative $(CO)_5W=NC_6H_5$ complex can behave as a nucleophile^{3a} or an electrophile,^{3b} the latter property is illustrated by reaction with PPh_3 to form $PhNPPH_3$. Our work has focused on preparing low-valent metal nitrene complexes containing strong π -acid ligands in the coordination sphere, features which may impart electrophilic character to nitrogen.⁶ This communication describes the simple amido (NH_2^-), imido (NH_2^-), and nitrido (N^{3-}) derivatives of the low-valent tungsten moiety $Tp'(CO)_2W$ (Tp' = hydrotris(3,5-dimethyl-1-pyrazolyl)borate) and their facile interconversions. The nitride complex serves as a convenient precursor to a variety of cationic nitrene complexes.

The preparation and reactions of these complexes are summarized in Scheme I. Treatment of a solution of $Tp'(CO)_2WI^7$ (1) with ammonia in CH_2Cl_2 at low temperature affords $Tp'(CO)_2W(NH_2)$ (2), a rare example of a metal complex with both carbonyl and amido ligands. Formulation of 2, which was isolated as a green solid, as an amido complex follows from the spectroscopic data.⁸ Two broad signals in the ¹H NMR spectrum (13.5 and 11.6 ppm) are assigned as the amido hydrogens and reflect restricted rotation around the $W=NH_2$ bond. These signals coalesce at 103 °C and establish the barrier to rotation as $\Delta G^\ddagger = 17$ kcal/mol.

Amido complex 2 shows ambiphilic character and reacts as either a hydride or proton donor. Thus, treatment of 2 with $[Ph_3C][PF_6]$ produces two isolable nitrene products [Tp' -

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(2) (a) Groves, J. T.; Takahashi, T. *J. Am. Chem. Soc.* 1983, 105, 2073. (b) Mahy, J.-P.; Bedi, G.; Battioni, P.; Mansuy, D. *J. Chem. Soc., Perkin Trans. 2* 1988, 1517.

(3) (a) Arndsten, B. A.; Sleiman, H. F.; Chang, A. K.; McElwee-White, L. *J. Am. Chem. Soc.* 1991, 113, 4871. (b) Sleiman, H. F.; Mercer, S.; McElwee-White, L. *J. Am. Chem. Soc.* 1989, 111, 8007.

(4) The Cu(I) aziridination catalysts reported by Evans may also involve an electrophilic nitrene intermediate: Evans, D. A.; Woerpel, K. A.; Hinman, M. M.; Faul, M. M. *J. Am. Chem. Soc.* 1991, 113, 726.

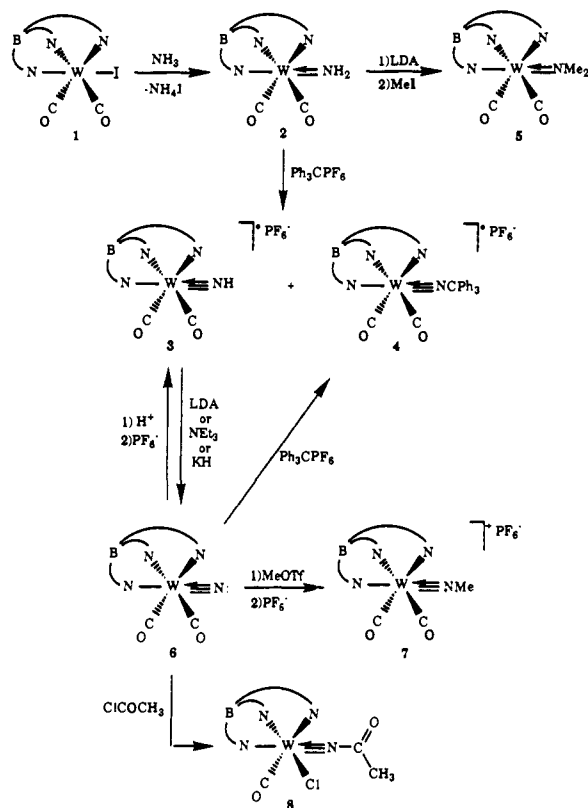
(5) Basolo has postulated the intermediacy of the electrophilic nitrene $[Ir(NH_2)_2NH]^+$ from protonation of $[Ir(NH_2)_2N_2]^{2+}$. See: (a) Lane, B. C.; McDonald, J. W.; Basolo, F.; Pearson, F. G. *J. Am. Chem. Soc.* 1972, 94, 3786. (b) Gafney, H. D.; Reed, J. L.; Basolo, F. *J. Am. Chem. Soc.* 1973, 95, 7998.

(6) Luan, L.; White, P. S.; Brookhart, M.; Templeton, J. L. *J. Am. Chem. Soc.* 1990, 112, 8190.

(7) Dicarboxyl 1 was prepared by heating a THF solution of $Tp'(CO)_2WI^6$ at reflux for several hours. The solvent was partially evaporated under vacuum. Orange crystals were obtained in 75% yield upon cooling the resulting red-orange solution overnight (-30 °C).

(8) Spectroscopic data for 2: IR (CH_2Cl_2) $\nu(CO)$ 1915, 1793 cm^{-1} ; IR Nujol mull $\nu(NH)$ 3395, 3305 cm^{-1} ; $\nu(BH)$ 2540 cm^{-1} ; ¹H NMR (400 MHz, CD_2Cl_2) δ 13.5 (br s, 1 H, NHH), 11.6 (br s, 1 H, NHH), 6.06, 5.90 (1:2, 3 CH), 2.53, 2.48, 2.41, 2.00 (6:3:3:6, 6 CH_3); ¹³C NMR (100 MHz, CD_2Cl_2) 254.7 (2 CO, $J_{WC} = 175$ Hz), 160.0, 151.2, 146.6, 145.6 (1:2:1:2, 6 CCH_3), 108.3, 106.6 (1:2, 3 CH), 15.5, 15.0, 13.0, 12.6 (1:2:1:2, 6 CH_3). Attempts to obtain an analytically pure sample were unsuccessful due to decomposition.

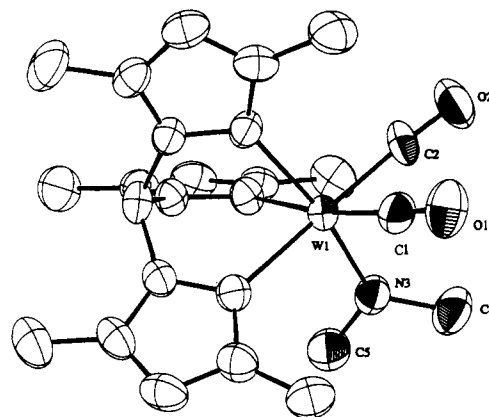
Scheme 1



(CO)₂W(NR)] [PF₆] (R = H, **3**; R = CPh₃, **4**) in a 4:1 ratio favoring the prototype nitrene complex **3**. The high $\nu(\text{CO})$ values for these dicarbonyl species (2092 and 2017 cm⁻¹ for **3** and 2083 and 2008 cm⁻¹ for **4**) suggest that the metal center is electron poor in these complexes. The nitrene group here formally acts as a four-electron-donor ligand in the neutral counting formalism or alternatively as a six-electron imido donor dianion.

The amido complex **2** also reacts with bases. Addition of excess lithium diisopropyl amide (LDA) or ^tBuLi to a cooled solution of **2** in THF produces an unstable orange solution ($\nu(\text{CO})$ at 1861 and 1724 cm⁻¹). Quenching this mixture with MeI affords the new amido species Tp'(CO)₂W(NMe₂) (**5**). Its ¹H NMR spectrum (CD₂Cl₂, 20 °C) shows distinct resonances for the amido methyl groups at 3.30 and 2.16 ppm. Figure 1 shows an ORTEP diagram of this complex.⁹ The WNMe₂ fragment is planar, and the angles around the nitrogen atom (W(1)–N(3)–C(4), 128.7 (5)°; W(1)–N(3)–C(5), 121.2 (4)°; C(4)–N(3)–C(5), 110.1 (6)°) are compatible with sp² hybridization. The W–N distance (1.956 (5) Å) falls in the range typical of metal–nitrogen multiple bonds.¹⁰ The acute angle between the two carbonyl ligands (C(1)–W(1)–C(2) = 71.8 (3)°) is compatible with optimal d π orbital interactions. Here the vertical NMe₂ fragment will donate into the lone vacant d π orbital, while the two filled d π orbitals will be preferentially stabilized by back-bonding to the two π -acid carbonyl ligands.¹¹

Reactions of the parent nitrene cation **3** with bases (KH, LDA, or NEt₃) lead to the deprotonated species Tp'(CO)₂W(N) (**6**), a nitrido tungsten(IV) compound which shows $\nu(\text{CO})$ absorptions

Figure 1. ORTEP diagram of Tp'(CO)₂W(NMe₂) (**5**).

at 2035 and 1938 cm⁻¹. Although attempts to isolate this product have failed due to decomposition during the workup, solution NMR and IR data support the above formulation.¹² Furthermore, the reactivity of this species confirms its composition. Reaction of nitride **6** with HBF₄ or [Ph₃C][PF₆] regenerates imido species **3** or **4**, respectively. This is consistent with basic character¹³ for the electron pair located at the nitride nitrogen in **6** and suggests that a variety of nitrene complexes can be prepared by treatment of **6** with electrophiles. Addition of electrophiles to terminal metal nitride units has precedent.¹⁴ Reaction of **6** with MeOSO₂CF₃, followed by counterion exchange, produces the related methyl nitrene complex [Tp'(CO)₂W(NMe)] [PF₆] (**7**) (see the scheme) with NMR resonances for the Tp' ligand similar to those observed for **3**, together with a methyl singlet at δ 3.67 ppm (³J_{WH} = 10 Hz). The three-bond tungsten–hydrogen coupling is a trademark for related tungsten nitrene complexes.

Addition of 1 equiv of ClC(O)CH₃ to a THF solution of nitride **6** at –50 °C produces the monocarbonyl complex Tp'(CO)–WCl(NC(O)CH₃) (**8**).¹⁵ This transformation may involve the intermediate [Tp'(CO)₂W(NCOCH₃)]Cl. We postulate that the strong electron-withdrawing COCH₃ group attached to nitrogen causes rapid CO loss to give an unsaturated monocarbonyl cation which is then trapped by chloride ion.

Acknowledgment. We are grateful to the National Institutes of Health (GM28938) and the Department of Energy (DE-FG05-85ER13430) for financial support. P.J.P. also thanks the Ministerio de Educacion y Ciencia (Spain) for a research studentship.

Supplementary Material Available: Details of the preparations of complexes **1**–**8**, Tables SI–SIII listing spectroscopic data for complexes **2**–**8**, and Tables SIV–SVII containing crystal collection data, bond distances and angles, atomic coordinates, and thermal parameters for **5** (12 pages); Table VIII listing observed and calculated structure factors for complex **5** (28 pages). Ordering information is given on any current masthead page.

(9) Crystal data for **5**: triclinic, $P\bar{1}$; $a = 11.151(4)$ Å, $b = 11.702(3)$ Å, $c = 10.391(4)$ Å, $\alpha = 93.46(3)^\circ$, $\beta = 108.56(3)^\circ$, $\gamma = 63.20(3)^\circ$, $Z = 2$. Diffraction data, collected at $T = 20$ °C, $\lambda = 0.70930$ Å: 5274 unique reflections with $2\theta < 55^\circ$ with 4208 considered observed, $\mu = 5.19$ mm⁻¹, transmission factors 0.31–0.43. Refinement data: $R = 0.039$, $R_w = 0.043$, goodness of fit = 1.25; highest final peak, 1.73 e/Å³; deepest hole, –1.45 e/Å³.

(10) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley-Interscience: New York, 1988.

(11) Templeton, J. L.; Winston, P. B.; Ward, B. C. *J. Am. Chem. Soc.* **1981**, *103*, 7713.

(12) Selected spectroscopic data for **6**: IR (THF) $\nu(\text{CO})$ 2035, 1938 cm⁻¹. A sample of **6** for NMR studies was prepared in situ by the addition of 1 equiv of Et₃N to a solution of **3** (25 mg, 0.035 mmol) in deuterated THF (0.4 mL). The ¹H NMR spectrum showed the disappearance of the broad signal at 11.0 (NH) in **3** and a new pattern for the Tp' protons: 6.05, 5.74 (2:1, 3 CH), 2.70, 2.40, 2.30, 2.22 (6:3:3:6, 6 CH₃). Diamagnetic behavior is consistent with the d² configuration placing both metal-based electrons in the single d π orbital lying between the two carbonyl ligands while the two d π orbitals directed toward the nitride (N³⁻) ligand are vacant.

(13) For structurally characterized nitrido complexes, see: (a) Reference 2a. (b) Groves, J. T.; Takadashi, T.; Butler, W. M. *Inorg. Chem.* **1983**, *22*, 884. (c) Hill, C. L.; Hollander, F. J. *J. Am. Chem. Soc.* **1982**, *104*, 7318.

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(15) Selected spectroscopic data for **8**: IR spectrum (THF) $\nu(\text{CO})$ 1948, $\nu(\text{C})$ 1682 cm⁻¹; ¹H NMR (400 MHz, C₆D₆) 1.73 (s, NC(O)CH₃); ¹³C{¹H} NMR (100 MHz, C₆D₆) 280.6 (CO, $J_{\text{WC}} = 177$ Hz), 180.9 ((NC(O)CH₃), ²J_{WC} = 35 Hz), 31.9 (NC(O)CH₃).}