tron-transfer reactivity in these systems. Picosecond flash photolysis studies on $M_2(dba)_3$ (M = Pd, Pt) and $Pd_2(dba\text{-}Fc)_3$ are in progress.

Acknowledgment. This research was supported by the NSERC and the FCAR. P.D.H. acknowledges Dr. D. James (Photon Technology Int.) for emission lifetime measurements and Mr. Yvon Couture (Université de Sherbrooke) for assistance in some of the electrochemical experiments.

---

[20] To whom correspondence should be addressed.

[21] Present address: Department of Chemistry, Beijing University, Beijing, China.

Département de chimie
Université de Sherbrooke
Sherbrooke, PQ, J1K 2R1 Canada

Pierre D. Harvey*,[20]
Liangbing Gan[21]

Received May 1, 1991

Reactions of Molybdenum(0) Tricarbonyl Complexes with 8-Azidoquinoline. Crystal Structure of the Phosphinimine Complex $Mo(CO)_4[N(PPh_3)(C_9H_6N)]$ and Evidence for a Bent Nitrene

The vast majority of monomeric, transition-metal nitrene (or imido) complexes that have been spectroscopically or structurally characterized are composed of high oxidation state metals with linear M–N–R units and triple bonds between M and N.[1] With the exception of several recent examples, the nitrene ligands in these complexes are very unreactive.[2] The bent M–N–R form, a geometry that is more rare, is predicted for low oxidation state metal complexes and/or when the formation of a triple bond between metal and nitrogen would violate the 18-electron rule.[3] Substantial bending of the M–N–R unit implies sp^2 hybridization at N, a M–N double bond, and a more nucleophilic nitrogen. Low-valent metal nitrene complexes have been proposed as transient intermediates in a variety of stoichiometric and catalytic reactions involving N–C or N–O bond cleavage and formation.[4] However, only recently has a tungsten(0) nitrene complex been trapped with triphenylphosphine to form the phosphinimine complex $(CO)_5W[N(PPh_3)Ph]$.[5]

Inspired by the work of Sloan and Thornton on high-valent metal nitrene complexes, we hypothesized that a low-valent transition-metal bent nitrene complex may be stabilized through incorporation of the nitrene into a chelate ring.[6] We chose 8-azidoquinoline because (1) formation of a nitrene ligand from the reaction of an organic azide with a metal complex is a common synthetic route for high oxidation state nitrene complexes[7] and (2) coordination of this ligand would produce a five-membered chelate ring incorporating a bent M═N—R unit. Herein we report the reactions of 8-azidoquinoline with *fac*-$Mo(CO)_3(CH_3CN)_2(L)$ [L = PPh_3 (**1a**), CH_3CN (**1b**), $P(OMe_3)_3$ (**1c**), $P(OEt_3)_3$ (**1d**)]. The crystal structure of $Mo(CO)_4[N(PPh_3)(C_9H_6N)]\cdot CH_3CN$ (**2**), containing a coordinated phosphinimine ligand, has been determined. A molybdenum(0)–bent nitrene appears to play a key role in the formation of the phosphinimine complex.

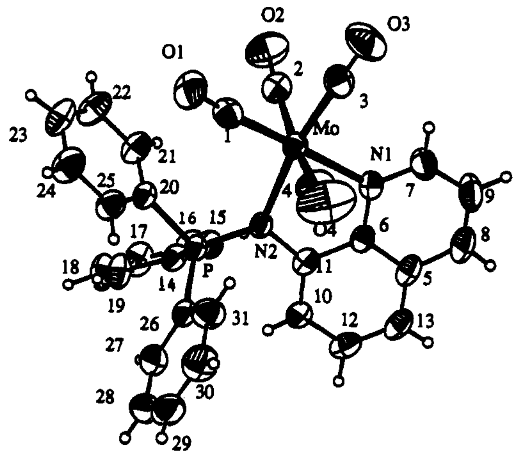


Figure 1. ORTEP drawing[16c] of $Mo(CO)_4(C_9H_6N_2)P(C_6H_5)_3\cdot CH_3CN$ (CH_3CN molecule omitted from the drawing). Thermal ellipsoids for non-hydrogen atoms are drawn at the 50% probability level; for hydrogen atoms the sphere radius is divided by 10. Carbon atoms are labeled by a single number (the same is used for the associated H atom, represented by a small circle). Selected bond lengths (Å): Mo–N(1), 2.245 (2); Mo–N(2), 2.312 (2); N(2)–P, 1.626 (2). Selected bond angles (deg): Mo–N(2)–P, 127.4 (1); Mo–N(2)–C(11), 113.9 (2); C(11)–N(2)–P, 117.9 (2).

Addition of **1a** in acetonitrile solution to 1 equiv of crystalline 8-azidoquinoline at −5 °C produces a dark red-brown solution within minutes.[8,9] After the solution was stirred at −5 °C for 1 h, the solution IR spectrum, at room temperature, reveals that the tricarbonyl pattern for **1a** (1925, 1818, 1799 cm^{-1}) has been replaced by a complex pattern of overlapping bands. The appearance of a band in the region just above 2000 cm^{-1} is suggestive of the formation of a cis-substituted tetracarbonyl species.[11] Also, the strong azide band, $\nu(N_3)$ at 2118 cm^{-1}, has completely dis-

---

[1] (a) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; John Wiley: New York, 1988. (b) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123.

[2] Recent examples of reactive nitrene complexes include $Cp_2Zr(NR)$,[2a] $Cp^*Ir(NR)$,[2b] and $[Tp'(CO)_2W(NR)]^+$ [Tp′ = hydridotris(3,5-dimethylpyrazolyl)borate].[2c] (a) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8729. (b) Glueck, D. S.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 2721. (c) Luan, L.; White, P. S.; Brookhart, M.; Templeton, J. L. *J. Am. Chem. Soc.* **1990**, *112*, 8190.

[3] Haymore, B. L.; Maatta, E. A.; Wentworth, R. A. D. *J. Am. Chem. Soc.* **1979**, *101*, 2063.

[4] (a) Nitta, M.; Kobayashi, T. *J. Chem. Soc., Perkin Trans. 1* **1985**, 1401. (b) Han, S. H.; Geoffroy, G. L. *Polyhedron* **1988**, *7*, 2331. (c) Hegedus, L. S.; Kramer, A. *Organometallics* **1984**, *3*, 1263. (d) Hegedus, L. S.; Lundmark, B. R. *J. Am. Chem. Soc.* **1989**, *111*, 9194. (e) Sleiman, H. F.; McElwee-White, L. *J. Am. Chem. Soc.* **1988**, *110*, 8700. (f) Pilato, L. S.; Williams, G. L. *Inorg. Chem.* **1988**, *110*, 3665. (g) Herndon, J. W.; McMullen, L. A. *J. Organomet. Chem.* **1989**, *368*, 83. (h) Peng, W.-J.; Gamble, A. S.; Templeton, J. L.; Brookhart, M. *Inorg. Chem.* **1990**, *29*, 463.

[5] Sleiman, H. F.; Mercer, S.; McElwee-White, L. *J. Am. Chem. Soc.* **1989**, *111*, 8007.

[6] Sloan, O. D.; Thornton, P. *Polyhedron* **1988**, *7*, 329. Another example of a high-valent, bent nitrene, where the nitrene is part of a chelate ring, has recently appeared: Minelli, M.; Carson, M. R.; Whisenhunt, Jr., D. W.; Imhof, W.; Huttner, G. *Inorg. Chem.* **1990**, *29*, 4801.

[7] Cenini, S.; La Monica, G. *Inorg. Chim. Acta* **1976**, *18*, 279. See also refs 1 and 3.

[8] 8-Azidoquinoline[8a] and **1a**[8b–d] are prepared according to published procedures. (a) The synthesis of aryl azides as reported by Smith and Brown (general procedure A) is used to prepare 8-azidoquinoline as pale yellow needles in 89% yield. Anal. Calcd (found) for $C_9H_6N_4$: C, 63.52 (63.56); H, 3.55 (3.46); N, 32.92 (32.55). Smith, P. A. S.; Brown, B. B. *J. Am. Chem. Soc.* **1951**, *73*, 2438. (b) Ross, B. L.; Grasselli, J. G.; Ritchey, W. M.; Kaesz, H. D. *Inorg. Chem.* **1963**, *2*, 1023. (c) Dobson, G. R.; Amr El Sayed, M. F.; Stolz, I. W.; Sheline, R. K. *Inorg. Chem.* **1962**, *1*, 526. (d) Tate, D. P.; Knipple, W. R.; Augl, I. M. *Inorg. Chem.* **1962**, *1*, 433.

[9] All reactions (excluding the preparation of 8-azidoquinoline) are done under N_2 by using standard Schlenk techniques.[10] Acetonitrile is dried in an inert atmosphere by refluxing over CaH_2. Photolysis experiments are carried out with Pyrex-filtered light from an Oriel 350-W high-pressure Hg arc lamp. Complex **1a** is prepared in situ by addition of 1 equiv of PPh_3 (129 mg, 0.5 mmol) to an CH_3CN solution of **1b** (generated by photolysis of 0.5 mmol of $Mo(CO)_6$ in 25–30 mL of CH_3CN). The solution of **1a** is cooled in an ice/salt bath (−5 °C) and added to 84 mg (0.5 mmol) of solid 8-azidoquinoline, also at −5 °C. Reactions are monitored in the IR region (at room temperature) by following the disappearance of the azide band [$\nu(N{=}N{=}N)$] at 2118 cm^{-1}, as well as changes in the metal carbonyl bands.

[10] Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*; John Wiley: New York, 1986.

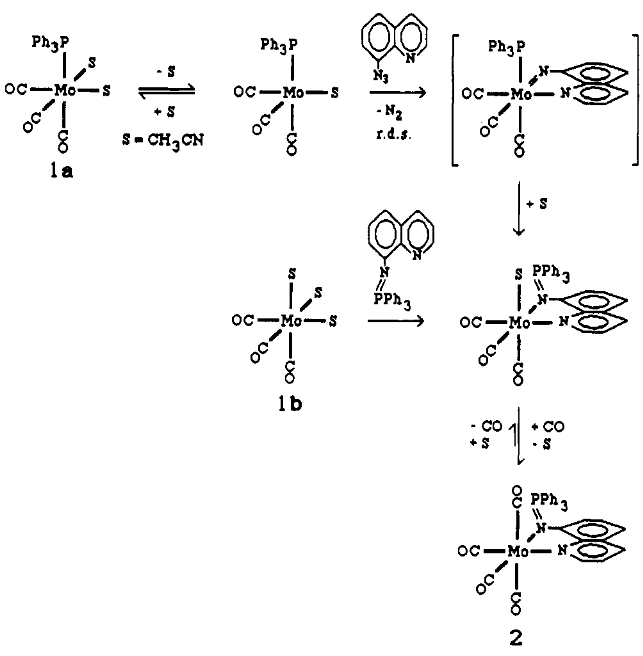
[11] (a) Cotton, F. A.; Kraihanzel, C. S. *J. Am. Chem. Soc.* **1962**, *84*, 4432. (b) Haas, H.; Sheline, R. K. *J. Chem. Phys.* **1967**, 2996. (c) Darensbourg, M. Y.; Darensbourg, D. *J. Chem. Ed.* **1970**, *47*, 33. (d) Brunner, H.; Herrmann, W. A. *Chem. Ber.* **1972**, *105*, 770. (e) tom Dieck, H.; Frans, K.-D.; Hohmann, F. *Chem. Ber.* **1975**, *108*, 163. (f) Kazlauskas, R. J.; Wrighton, M. S. *J. Am. Chem. Soc.* **1982**, *104*, 5784.

0020-1669/91/1330-3241$02.50/0

appeared. The reaction mixture is filtered, concentrated, and placed in the freezer.[12] After 48 h of cooling, red-brown crystals are isolated by filtration in 20% yield. Key features in the spectroscopic data that establish the identity of the crystalline product as the tetracarbonylmolybdenum phosphinimine complex, **2**, are as follows.[13] The ^{1}H NMR spectrum reveals a characteristic set of resonances for the quinoline ring and a complex multiplet for PPh_3 in the expected 6/15 ratio. There is a single sharp resonance in the ^{31}P NMR spectrum at +27.8 ppm. The solid-state IR spectrum is characteristic of a cis-substituted tetracarbonylmolybdenum(0) complex, and there is no N-H stretch. The P-N stretch could not be positively identified; however, there are several prominent bands in the appropriate region (1350–1100 cm^{-1}) that do not appear in the solid-state IR spectra of PPh_3, 8-azidoquinoline, or 8-aminoquinoline.[14] The base peak in the FAB-MS is for the phosphinimine ligand ($C_9H_6N_2P(C_6H_5)_3^+$; *m/z* 405), and there are also several clusters of weaker peaks at higher mass/charge due to the parent ion ($[Mo(CO)_4(C_9H_6N_2)P(C_6H_5)_3]^+$; *m/z* 613) and ions resulting from successive loss of CO from the parent.

The X-ray structure of **2**·CH_3CN was obtained, and an ORTEP diagram of **2** is shown in Figure 1.[15] The solid-state structure confirms the assignment made by spectroscopy. The Mo coordination sphere is slightly distorted from an ideal octahedron, with trans angles ranging 166.0–176.4° and cis angles 72.7–106.1°. The largest distortions appear to result from the bite of the phosphinimine ligand and the steric bulk of triphenylphosphine (e.g., N(1)–Mo–N(2) = 72.7° and C(1)–Mo–N(2) = 106.1°). Both Mo–N distances are within the range expected for single bonds; the Mo–phosphinimine nitrogen bond (Mo–N(2) = 2.312 (2) Å) is slightly longer than the Mo–quinoline nitrogen bond (Mo–N(1) = 2.245 (2) Å).[18] The P–N(2) bond distance, 1.626 (4) Å, is indicative of a π interaction between P and N.[19] The bond angles around N(2) average 120°; however, the strain induced by the chelate and the bulky phosphine is evident in the Mo–N(2)–P (127.4°) and Mo–N(2)–C(11) (113.9°) angles.

Scheme I



Structurally characterized transition-metal complexes containing the phosphinimine ligand (RN=PR'$_3$) are rare. Selected structural parameters for phosphinimine complexes where R = H, C, or Si are listed in supplementary material Table I. As has been previously noted, since the R group in phosphinimines is frequently Si or H, the limited number of phosphinimine complexes is a result of lability of N–Si and N–H bonds.[22] In the case of **2**, the phosphinimine nitrogen is bonded to C and the chelated quinoline ring contributes to molecular stability.

Two other products in the reaction of **1a** with 8-azidoquinoline have been identified as $Mo(CO)_3(PPh_3)[N(PPh_3)(C_9H_6N)]$ (**3**) and $Mo(CO)_3(PPh_3)_2(CH_3CN)$ (**4**).[24] The overall yield based on Mo is 50%, and the approximate molar ratio of the three complexes is 1/1/0.1 (**2**/**3**/**4**).[25] Formation of the phosphinimine ligand is significant because it suggests the intermediacy of a molybdenum nitrene complex. While we have not yet succeeded in spectroscopically characterizing or isolating the molybdenum nitrene intermediate, the following experiments led us to conclude that a nitrene complex plays a key role in the reaction.

Formation of the phosphinimine ligand could occur outside the coordination sphere of the metal by reaction of free PPh_3 with

---

(12) A finely divided black solid forms during the reaction that we have not been able to characterize because of its low solubility. The solid-state IR spectrum of this precipitate has one very broad band in the molybdenum carbonyl region and aromatic bands characteristic of the quinoline ring.

(13) Spectroscopic and analytical data for **2**: ^{1}H NMR (200 MHz in CD_2Cl_2): δ 6.45 (dt, 1 H), 6.85 (t, 1 H), 7.10 (dd, 1 H), 7.32 (dd, 1 H), 7.85–7.47 (m, 15 H, PPh_3), 8.10 (dd, 1 H), 9.14 ppm (dd, 1 H); $^{31}P\{^1H\}$ NMR (81 MHz in CD_2Cl_2) 27.8 ppm (s); IR (Nujol) ν(Mo–CO) 2000, 1886, 1859, 1820 cm^{-1} and prominent bands associated with the phosphinimine ligand 1306 (s), 1266 (s), 1111 (vs), 963 cm^{-1} (m). Anal. Calcd (found) for $Mo(CO)_4(C_9H_6N_2)P(C_6H_5)_3 \cdot CH_3CN$: C, 60.65 (60.40); H, 3.70 (3.73); N, 6.43 (6.32).

(14) (a) Wiegräbe, W.; Bock, H.; Lüttke, W. *Chem. Ber.* **1966**, *99*, 3737. (b) Bock, H.; tom Dieck, H. *Z. Naturforsch. B* **1966**, *21*, 739.

(15) Crystals of **2** were obtained by cooling an acetonitrile solution of the reaction mixture for 2 days. A red-brown crystal was selected and sealed under N_2 in a glass capillary. Crystal data: $Mo(CO)_4(C_9H_6N_2)P(C_6H_5)_3 \cdot CH_3CN$, M_n = 653.2, triclinic, space group $P\bar{1}$, a = 9.260 (5) Å, b = 12.390 (6) Å, c = 13.729 (7) Å, α = 99.43 (3)°, β = 92.56 (3)°, γ = 108.21 (3)°, V = 1468 (4) Å^3, Z = 2, μ(Mo Kα) = 4.97 cm^{-1}, $F(000)$ = 332, ρ_{calcd} = 1.47 g/cm^3. Data collection was performed at 298 K on a Siemens AED2 diffractometer operating in the ω–θ mode and with Mo Kα radiation (λ = 0.71069 Å, graphite monochromator). The total number of unique reflections was 6723, of which 3725 have $|F| \geq 6.0\sigma(|F|)$. No absorption corrections were made owing to the small absorption coefficient and the ill-defined shape of the crystal. The 2θ range for data collection was $3° < 2\theta < 50°$. Only one independent set of reflections was collected: $-12 \leq h \leq +12, -16 \leq k \leq +16, 0 \leq l \leq +17$. No extinction was detected. All non-hydrogen atoms were found by using SHELX-86.[16a,b] Scattering factors and anomalous scattering factors were taken from ref 16d. All hydrogen atoms were located on successive electron density maps. The full least-squares refinement on F (SHELX 76[17]), with anisotropic thermal parameters for all non-hydrogen atoms, converged to R = 0.0265 and R_w = 0.0266 for 452 variables.

(16) (a) Sheldrick, G. M. In *Crystallographic Computing 3: Data Collection, Structure Determination, Proteins and Databases*; Sheldrick, G. M., Kruger, C., Goddard, R., Eds.; Clarendon Press: Oxford, England, 1985; pp 184–189. (b) Robinson, W. T.; Sheldrick, G. M. In *Crystallographic Computing 4: Techniques and New Technologies*; Isaacs, N. W., Taylor, M. R., Eds.; International Union of Crystallography, University Press: Oxford, England, 1988; pp 366–377. (c) Johnson, C. K. ORTEP Report ORNL-3794. Oak Ridge National Laboratory: Oak Ridge, TN, 1965. (d) Cromer, D. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(17) Sheldrick, G. M. SHELX 76; Program for Crystal Structure Determination. University of Cambridge, 1976.

(18) For example, the Mo–N bond in $Mo(CO)_3L$ (L = *cis*-diethylenetriamine) is 2.32 Å: Dahl, L. *J. Less-Common Met.* **1974**, *36*, 255.

(19) P–N double bonds have been reported in the range 1.51–1.64 Å, and single bonds generally fall in the range 1.71–1.78 Å. See: Armitage, F. *Inorganic Rings and Cages*; Edward Arnold: London, 1972; pp 289–291 and refs 20–23.

(20) Maurer, A.; Fenske, D.; Beck, J.; Hiller, W.; Strähle, J.; Böhm, E.; Dehnicke, K. *Z. Naturforsch., B* **1988**, *43*, 5.

(21) Fenske, D.; Böhm, E.; Dehnicke, K.; Strähle, J. *Z. Naturforsch., B.* **1988**, *43*, 1.

(22) Cramer, R. E.; Roth, S.; Gilje, J. W. *Organometallics* **1989**, *8*, 2327.

(23) Adamson, G. W.; Bart, J. C. *J. Chem. Soc. A* **1970**, 1452.

(24) Spectroscopic data for **3**: IR (Nujol) ν(Mo–CO) 1904, 1809, 1757 cm^{-1}; ^{1}H NMR (200 MHz in CD_2Cl_2) δ 6.33 (dt, 1 H), 6.67 (t, 1 H), 6.86 (m, 2 H), 7.64–7.0 (m, 30 H, PPh_3), 7.76 (dd, 1 H), 8.80 ppm (dd, 1 H); $^{31}P\{^1H\}$ NMR (81 MHz in CD_2Cl_2) 32.0 (s, br), 30.7 ppm (s). Complex **4** was independently prepared by addition of 2 equiv of PPh_3 to a CH_3CN solution of **1c**. Spectroscopic data for **4**: IR (Nujol) ν(Mo–CO) 1931, 1835, 1810 cm^{-1}; $^{31}P\{^1H\}$ NMR (81 MHz in CD_2Cl_2) +27.8 ppm (s).

(25) Complexes **2**–**4** are isolated by workup of the reaction mixture at room temperature. Absolute yields were not determined due to difficulties in separating the complexes; an approximate molar ratio was estimated from IR and ^{1}H NMR spectra.

8-azidoquinoline. This is unlikely for two reasons. First, there is no excess PPh_3 present in the reaction of **1a** with azide and, second, reactions of phosphines with organic azides generally require elevated temperatures.[26] In fact, at room temperature, the reaction of PPh_3 with 1 equiv of 8-azidoquinoline in CH_3CN solution proceeds very slowly; only 30% of the azide reacts in 1 h.[27] In contrast the reaction of 8-azidoquinoline with an CH_3CN solution of **1a** is complete in $^1/_2$ h at room temperature. We have also determined that 8-azidoquinoline reacts rapidly with molybdenum(0) carbonyl complexes in the absence of coordinated phosphine. Addition of an acetonitrile solution of **1b** to 1 equiv of 8-azidoquinoline at −5 °C produces a deep purple solution. The room-temperature IR spectrum of the reaction mixture consists of many overlapping bands in the carbonyl region, but the absence of the $\nu(N_3)$ band confirms that the azide has reacted. (It should be noted that in the absence of molybdenum, 8-azidoquinoline is stable in CH_3CN solution for at least 24 h.[28]) Addition of 1 equiv of PPh_3 to the purple solution formed by addition of 8-azidoquinoline to **1b** at low temperature yields the same mixture of products (**2**–**4**) as obtained by addition of **1a** to 8-azidoquinoline. We therefore conclude that formation of the phosphinimine ligand is metal-mediated.

Preliminary kinetic experiments indicate that reaction of **1a** with 8-azidoquinoline in CH_3CN solution at 25 °C is first order in **1a** and first order in azide.[29] The kinetic data eliminates the possibility that formation of a free nitrene via loss of N_2 from azide is the rate-determining step. Octahedral, d^6 transition-metal complexes generally react via dissociative mechanisms.[30] Since measurements were made in CH_3CN, the kinetics can be explained by a rapid preequilibrium step preceding the rate-determining step.

We suggest that reaction of **1a** with 8-azidoquinoline proceeds via initial dissociation of an CH_3CN ligand, followed by coordination of 8-azidoquinoline in the rate-determining step forming a molybdenum nitrene complex (see Scheme I).[31] Not surprisingly, the nitrene complex is very reactive and we have not yet succeeded in isolating it. However, it can be trapped by phosphine supplied by **1a** in an intra- or intermolecular step to form the phosphinimine ligand.

One crucial step in the production of **2** is addition of a fourth carbonyl ligand. In the absence of CO the yield of the tetracarbonyl complex, **2**, is low (ca. 20%, based on azide reacted). However, addition of CO to an CH_3CN solution of **1a** and azide at −5 °C increases the isolated yield of **2** to approximately 60% (based on azide reacted). Formation of **2** is not complete, even in the presence of excess CO, because **1a** reacts with CO to form $Mo(CO)_4(PPh_3)(CH_3CN)$, which does not react with 8-azidoquinoline.[32]

In the absence of CO, the phosphinimine solvento complex $Mo(CO)_3(CH_3CN)[N(PPh_3)(C_9H_6N)]$ is observed in the IR spectrum during the reaction of **1a** with 8-azidoquinoline. The phosphinimine solvento complex can be prepared independently by reaction of **1b** with $Ph_3P{=}NR$ (R = quinoline).[33] Under 1 atm of CO, the phosphinimine solvento complex reacts quickly and cleanly to form **2**. When **2** is dissolved in CH_3CN, in the absence of CO, an equilibrium between **2** and the phosphinimine solvento complex is established (see Scheme I).

Changing the phosphine ligand in **1** alters the course of the reaction. For example, reaction of the phosphite-substituted complexes $Mo(CO)_3(CH_3CN)_2(PR_3)$ (**1c**, R = OMe; **1d**, R = OEt) and 8-azidoquinoline in CH_3CN solution does not lead to formation of the analogous phosphitimine products. Identification of the primary reaction products as the amine complexes $Mo(CO)_3(PR_3)[H_2N(C_9H_6N)]$ (**5a**, R = OMe; **5b**, R = OEt) is made by comparison to authentic samples prepared from **1c** or **1d** and 8-aminoquinoline.[34] Organic nitrenes, generated in situ, can abstract hydrogen atoms to form amides and amines;[26] however, we have shown that in CH_3CN solution, 8-azidoquinoline does not form 8-aminoquinoline in the absence of molybdenum.[28] We suggest that reactions of **1c** and **1d** with 8-azidoquinoline also proceed through molybdenum nitrenes and speculate that the greater lability of the Mo–PPh_3 bond relative to the Mo–$P(OR)_3$ bond is responsible for the difference in product formation, i.e., **2** vs **5a** or **5b**.[35] The source of hydrogen in **5a** and **5b** appears to be from adventitious water in the solvent.[36] We are continuing to investigate the mechanism of formation of the phosphinimine and amine ligands in these reactions. Our goal is to isolate or spectroscopically characterize the molybdenum(0) nitrene intermediate and to investigate its reactivity toward other substrates.

Acknowledgment is made to the University of Maine Faculty Research Fund, the National Science Foundation, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We thank Dr. Robert J. Anderegg (Glaxo, Inc.) for FAB-MS experiments and for helpful discussions. Ms. S. Brackett and Mr. L. Lester are acknowledged for mass spectra and ^{31}P NMR spectra obtained at the University of Maine.

Supplementary Material Available: Tables of crystallographic data, including atomic coordinates, thermal anisotropic parameters, bond lengths and angles, and selected structural parameters for phosphinimine complexes where R = H, C, or Si (Table I) (6 pages); a table of observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

---

(26) Scriven, E. F. V., Ed. *Azides and Nitrenes, Reactivity and Utility*; Academic Press: New York, 1984.

(27) The extent of reaction is determined by monitoring the disappearance of the $\nu(N_3)$ band.

(28) At room temperature, under room lights, there is no decrease in the azide band at 2118 cm^{-1} over a 24-h period. Sampling the solution for mass spectra (EI) reveals parent ion peaks at m/z 170 (N_3R^+) and 142 ($N_3R^+ - N_2$). Analysis of solid 8-azidoquinoline by EI-MS reveals the same parent ions.

(29) The rate of disappearance of the azide band, $\nu(N_3)$ at 2118 cm^{-1}, was measured as a function of concentration of **1a** and 8-azidoquinoline: [**1a**] = 0.056–0.113 mM; [azide] = 0.113–0.226 mM. All kinetic measurements were conducted in a glovebox by using a Midac FTIR instrument. Collection of data was facilitated by the use of Spectra Calc software.

(30) Langford, C. H.; Gray, H. B. *Ligand Substitution Processes*; W. A. Benjamin, Inc.: Reading, MA, 1966.

(31) Transition-metal-mediated decomposition of organic azides via nitrene intermediates has been proposed previously. See for example: Dekker, M.; Knox, G. R. *J. Chem. Soc., Chem. Commun.* **1967**, 1243. Campbell, C. D.; Rees, C. W. *J. Chem. Soc., Chem. Commun.* **1969**, 537.

(32) 8-Azidoquinoline does not react with the monoacetonitrile complexes $Mo(CO)_4(PPh_3)(CH_3CN)$, $Mo(CO)_3(PPh_3)_2(CH_3CN)$, or $Mo(CO)_3(dppe)(CH_3CN)$.

(33) $Mo(CO)_3(CH_3CN)[N(PPh_3)(C_9H_6N)]$ is prepared at room temperature by addition of a CH_2Cl_2 solution of $(Ph_3P)N(C_9H_6N)$ to an CH_3CN solution of **1b**. IR: ν(CO) 1900, 1780, 1761 cm^{-1}. Passing CO through the solution for 2 min results in the complete conversion of the phosphinimine solvento complex to **2**. The phosphinimine ligand was prepared by stirring PPh_3 with 8-azidoquinoline in CH_3CN for 24 h at 50 °C, followed by recrystallization from CH_2Cl_2. Anal. Calcd (found) for $(Ph_3P)N(C_9H_6N)$: C, 80.18 (79.45); H, 5.23 (5.10); N, 6.93 (6.72). IR (Nujol): 1327, 1124, 1107, 978 cm^{-1}. $^{31}P\{^1H\}$ NMR (81 MHz in CD_2Cl_2): +5.1 ppm (s).

(34) Complexes **5a** and **5b** are prepared by reaction of **1c** or **1d** with 1 molar equiv of 8-aminoquinoline in CH_3CN solution. **5a** and **5b** are extremely air-sensitive red-brown solids. An X-ray crystal structure analysis of **5a** is currently underway. Spectroscopic data for **5a**: IR (Nujol) ν(Mo–CO) 1926, 1821, 1785 cm^{-1}, ν(N–H) 3317, 3267 cm^{-1}; ^1H NMR (200 MHz in CD_2Cl_2) δ 3.45 (d, 9 H), 4.78 (b, 2 H), 7.32–7.78 (m, 4 H), 8.19 (dt, 1 H), 9.29 ppm (dt, 1 H). IR for **5b** (Nujol): ν(Mo–CO) 1925, 1817, 1761 cm^{-1}; ν(N–H) 3317, 3269 cm^{-1}.

(35) Howell, J. A. S.; Burkinshaw, P. M. *Chem. Rev.* **1983**, *83*, 557.

(36) We have compared the rate of reaction of **1c** with 8-azidoquinoline in CD_3CN without added H_2O (containing 60 mM H_2O as received) and in CD_3CN with added H_2O (145 mM total H_2O) by ^1H NMR spectroscopy. In the reaction mixture containing 145 mM H_2O, the rate of disappearance of 8-azidoquinoline is greatly accelerated and the rate of appearance of free aminoquinoline is approximately doubled. A control experiment establishes that **5a** rapidly decomposes in wet CD_3CN to yield free 8-aminoquinoline.

Laboratoire des Fluorures-UA CNRS 449
Faculté des Sciences-Université du Maine
72017 Le Mans Cedex, France
J. L. Fourquet
M. Leblanc

Department of Chemistry
University of Maine
Orono, Maine 04469
A. Saravanamuthu
M. R. M. Bruce*
A. E. Bruce*

Received December 28, 1990