bar was charged with sodium borohydride (0.38 g, 10 mmol) and cooled to 0 °C. A 3.0 M THF solution of pentafluorophenol (10 mL, 30 mmol) was added slowly with constant stirring. Hydrogen evolution was rapid and was essentially complete at 3 h at 0 °C. The reaction mixture was left aside for an additional 9 h to ensure complete reaction. A 1.0-mL aliquot of the clear solution containing the product, $NaBH(OC_6F_5)_3$, gave on hydrolysis 0.96 mmol (100%) of hydrogen. A ^{11}B NMR spectrum of the clear reaction solution showed a single signal: δ 5.8 (d, J = 120 Hz). No signals attributable to the presence of $NaBH_4$ in the solution could be detected by ^{11}B NMR spectroscopy.

Registry No. MeOH, 67-56-1; C_6H_5OH, 108-95-2; C_6F_5OH, 771-61-9; $NaBH_3(OMe)$, 18253-42-4; $NaBH(OMe)_3$, 16940-17-3; $NaBH(OC_6H_5)_3$, 139494-69-2; $NaBH(OC_6F_5)_3$, 139494-70-5; $NaB(OMe)_4$, 18024-69-6; $NaBH_4$, 16940-66-2; trifluoroethanol, 75-89-8; hexafluoro-2-propanol, 920-66-1; sodium (trifluoroethoxy)borohydride, 139494-66-9; sodium tris(trifluoroethoxy)borohydride, 139494-67-0; sodium tris(hexafluoro-2-propanoxy)borohydride, 139494-68-1; sodium tetrakis(trifluoroethoxy)borohydride, 139494-71-6.

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Preparation and Reactivity of Molybdenum Hydride and Phenyldiazene Complexes

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Introduction

We are interested in studying the fundamental reaction chemistry of a class of simple nitrogen-containing molecules, the monosubstituted diazenes (NH=NR). Although NH=NR compounds are very reactive and generally decompose at low temperatures with loss of N_2,[1] the coordination chemistry of these molecules is extensive, and thermally stable aryldiazene complexes have been prepared for various metals including Pt, Fe, Ru, Os, Rh, Ir, Mn, Re, and W.[2,3] The two most general synthetic routes to M(NH=NR) complexes, 1,1-insertion of arenediazonium cations into M–H bonds and oxidation of coordinated hydrazine ligands, are complementary since the former method is limited to aryl derivatives (but ^{15}N and ^2H isotopic labeling is trivial),[2] while the latter method allows extension to alkyl (and even the parent, NH=NH) systems.[3] Clearly, the complexed diazenes can be studied to some degree while still attached to the metals, but we have been exploring systems where these ligands can be freed from the coordination sphere at low temperatures, allowing their study as the free molecules in solution.[4]

The discovery that bromide ions smoothly displace the NH=NPh ligand from [*trans*,*trans*-W(NH=NPh)$(CO)_2$(NO)$(PPh_3)_2^+$] at ~0 °C sparked our initial studies into the subsequent chemistry of the very reactive NH=NPh molecule.[4a,b] However, NH=NPh is only marginally stable at the temperature of the displacement reaction ($t_{1/2}$ ~ 85 min at 5 °C), and other aryl and alkyl derivatives are even more thermally sensitive.[1,5] We thus set out to prepare analogous molybdenum diazene complexes with the hope that displacement reactions from this second transition-series metal could be effected at lower temperatures than for the third-row W species. Herein we report the synthesis of a Mo(NH=NPh) complex and its reactivity with respect to displacement of the NH=NPh ligand.

Experimental Section

Dry, oxygen-free solvents and standard high-vacuum and Schlenk techniques were used throughout. $[NO][AlCl_4]$ was obtained from the reaction of NOCl with $AlCl_3$.[6] *trans*-Mo$(ClAlCl_3)$(NO)$(CO)_4$ (**1**) was prepared from $Mo(CO)_6$ and $[NO][AlCl_4]$, and *trans*,*trans*-Mo(Cl)$(CO)_2$(NO)$(PPh_3)_2$ (**2a**) was prepared from **1** and PPh_3, according to literature procedures;[7] *trans*,*trans*-Mo(Cl)$(CO)_2$(NO)$(PCy_3)_2$ (**2b**) was analogously prepared from **1** and PCy_3 (Cy = c-C_6H_{11}).

Preparation of *trans*,*trans*-Mo(H)$(CO)_2$(NO)$(PPh_3)_2$ (3a). A 3.00-g (4.04-mmol) sample of *trans*,*trans*-Mo(Cl)$(CO)_2$(NO)$(PPh_3)_2$, 6.99 g (26.7 mmol) of triphenylphosphine, and 0.352 g (16.2 mmol) of lithium borohydride were placed in a 100-mL flask attached to a needle valve. The flask was evacuated and cooled in a −78 °C bath, and then 70 mL of THF was vacuum transferred onto the solids. The flask was placed under positive argon pressure and was slowly warmed to near reflux for 40 min, during which time the yellow mixture turned magenta in color and became homogeneous. The flask was removed from the argon manifold, and the solution was filtered through Celite. The filtrate volume was reduced to 15 mL on a rotary evaporator, and then 50 mL of hot EtOH was added to the solution dropwise to precipitate the product. The hot mixture was filtered, and the orange solids were sequentially washed with boiling EtOH (3 × 70 mL) and Et_2O (50 mL). The product was dried in vacuo to give 1.97 g (69% yield). The crude product can be conveniently recrystallized from CH_2Cl_2/petroleum ether to give a bright yellow powder; the recrystallized material was used in all subsequent reactions. Anal. Calcd for $C_{38}H_{31}NO_3P_2Mo$: C, 64.51; H, 4.42; N, 1.98. Found: C, 64.01; H, 4.52; N, 1.87.

***trans*,*trans*-Mo(H)$(CO)_2$(NO)$(PCy_3)_2$ (3b)** was prepared analogously from **2b** in 57% yield (using PCy_3 instead of PPh_3 in the lithium borohydride reduction).

Preparation of *trans*,*trans*-Mo(η^1-OSO_2CF_3)$(CO)_2$(NO)$(PPh_3)_2$ (4a). A 0.27-mL volume of triflic acid was added via syringe to a stirred CH_2Cl_2 solution of Mo(H)$(CO)_2$(NO)$(PPh_3)_2$ (2.00 g) at −78 °C. The orange solution was slowly warmed to ambient temperature with concomitant gas evolution (H_2). The resulting yellow solution was filtered, and the product was precipitated as lemon-yellow microcrystals by addition of Et_2O/petroleum ether. The product was washed with petroleum ether and dried in air to give 1.79 g (74% yield) of the triflate complex. Anal. Calcd for $C_{39}H_{30}NO_6F_3P_2SMo$: C, 54.75; H, 3.53; N. 1.64. Found: C, 54.61; H, 3.39; N. 1.78.

***trans*,*trans*-Mo(η^1-OSO_2CF_3)$(CO)_2$(NO)$(PCy_3)_2$ (4b)** was similarly prepared by the action of triflic acid on **3b** in 41% yield. Anal. Calcd for $C_{39}H_{66}NO_6F_3P_2SMo$: C, 52.52; H, 7.46; N, 1.57. Found: C, 53.09; H, 7.70; N, 1.89.

Preparation of [*trans*,*trans*-Mo(NH=NPh)$(CO)_2$(NO)$(PPh_3)_2$][PF_6] (5). A 74-mg (0.30-mmol) amount of $[PhN_2][PF_6]$ was added to 200 mg (0.28 mmol) of **3a** in 5 mL of acetone. The yellow suspension rapidly turned homogeneous and deep red (<5 min). The solution was filtered and the volume was reduced to 2 mL, and then Et_2O was added dropwise until precipitation began. Petroleum ether (5 mL) was added to complete precipitation of the bright orange microcrystals, which were filtered off and washed with 20 mL of petroleum ether, affording 222 mg (82% yield) of product. Anal. Calcd for $C_{44}H_{36}N_3O_3F_6P_3Mo$: C, 55.19; H, 3.79; N, 4.39. Found: C, 55.39; H, 3.77; N, 4.26.

[*trans*,*trans*-Mo(^{15}NH=^{15}NPh)$(CO)_2$(NO)$(PPh_3)_2$][PF_6] (5-$^{15}N_2$) was prepared analogously from **3a** and $[Ph^{15}N_2][PF_6]$.

Preparation of *trans*,*trans*-Mo(Br)$(CO)_2$(NO)$(PPh_3)_2$ (6). On a frit assembly, 5 mL of methylene chloride was transferred at −78 °C onto a mixture of 200 mg (0.234 mmol) of **4a** and 79 mg (0.25 mmol) of [n-Bu_4N][Br] in a 25-mL flask. The solution was warmed to ambient temperature and stirred for 5 min. Absolute ethanol (5 mL) was added by syringe to the mixture, and then the solvent volume was reduced in vacuo to precipitate the yellow product. The mixture was filtered, and

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(1) (a) Kosower, E. M. *Acc. Chem. Res.* **1971**, *4*, 193. (b) Kosower, E. M.; Huang, P. C. *J. Am. Chem. Soc.* **1968**, *90*, 2367. (c) Tsuji, T.; Kosower, E. M. *Ibid.* **1971**, *93*, 1992.

(2) Typical examples of insertion reactions with metal hydrides that give coordinated NH=NR include: (a) Parshall, G. W. *J. Am. Chem. Soc.* **1967**, *89*, 1822. (b) Parshall, G. W. *Ibid.* **1965**, *87*, 2133. (c) Haymore, B. L.; Ibers, J. A. *Ibid.* **1975**, *97*, 5369. (d) Albertin, G.; Antoniutti, S.; Lanfranchi, M.; Pelizzi, G.; Bordignon, E. *Inorg. Chem.* **1986**, *25*, 950 (and references therein).

(3) For examples of oxidations of hydrazines to give coordinated NH=NR, see: (a) Diels, O.; Koll, W. *Liebigs Ann.* **1925**, *443*, 262. (b) Petredis, D.; Burke, A.; Balch, A. L. *J. Am. Chem. Soc.* **1970**, *92*, 428. (c) Sellmann, D.; Böhlen, E.; Waeber, M.; Huttner, G.; Zsolnai, L. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 981. (d) Sellman, D.; Soglowek, W.; Knoch, F.; Moll, M. *Ibid.* **1989**, *28*, 1271. (e) Ackermann, M. N.; Willett, R. M.; Englert, M. H.; Barton, C. R.; Shewitz, D. B. *J. Organomet. Chem.* **1979**, *175*, 205. (f) Ackermann, M. N.; Dobmeyer, D. J.; Hardy, L. C. *Ibid.* **1979**, *182*, 561. (g) Sellmann, D.; Gerlach, R.; Jödden, K. *Ibid.* **1979**, *178*, 433. (h) Sellmann, D.; Jödden, K. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 464.

(4) (a) Smith, M. R., III; Hillhouse, G. L. *J. Am. Chem. Soc.* **1988**, *110*, 4066. (b) Smith, M. R., III; Hillhouse, G. L. *Ibid.* **1989**, *111*, 3764. (c) Smith, M. R., III; Keys, R. L.; Hillhouse, G. L.; Rheingold, A. L. *Ibid.* **1989**, *111*, 8312.

(5) Smith, M. R., III; Hillhouse, G. L. Unpublished results.

(6) Partington, J. R.; Whynes, A. L. *J. Chem. Soc.* **1948**, 1952.

(7) Seyferth, K.; Taube, R. *J. Organomet. Chem.* **1982**, *229*, 275.

0020-1669/92/1331-1535$03.00/0

Table I. NMR and Infrared Spectroscopic Data

compd	type	data[a]
trans-Mo(CO)$_4$(NO)(ClAlCl$_3$) (**1**)	IR	ν_{CO} = 2078 (vs); ν_{NO} = 1745 (s)
trans,*trans*-Mo(Cl)(CO)$_2$(NO)(PPh$_3$)$_2$ (**2a**)	^{1}H	7.65–7.62 (m, 12 H, Ph), 7.39–7.31 (m, 18 H, Ph)
	^{31}P{^{1}H}	33.3 (s)
	IR	ν_{CO} = 1962 (vs), 2044 (w); ν_{NO} = 1637 (s)
trans,*trans*-Mo(Cl)(CO)$_2$(NO)(PCy$_3$)$_2$ (**2b**)	^{1}H	2.23 (m, Cy, 6 H), 2.07 (m, Cy, 12 H), 1.87 (m 12 H), 1.72 (s (br), Cy, 6 H), 1.56 (m, Cy, 12 H), 1.30 (s (br), Cy, 18 H)
	^{31}P	37.6 (s)
	IR	ν_{CO} = 1940 (vs), 2025 (w); ν_{NO} = 1624 (s)
trans,*trans*-Mo(H)(CO)$_2$(NO)(PPh$_3$)$_2$ (**3a**)	^{1}H	7.71–7.56 (m, Ph, 12 H), 7.40–7.30 (m, Ph, 18 H), −1.43 (t, Mo–*H*, $^2J_{PH}$ = 25.7 Hz, 1 H)
	^{31}P{^{1}H}	51.3 (s)
	IR	ν_{CO} = 1931 (vs), 2010 (w); ν_{NO} = 1653 (s)
trans,*trans*-Mo(H)(CO)$_2$(NO)(PCy$_3$)$_2$ (**3b**)	^{1}H	2.45–2.40 (m, Cy, 6 H), 2.18–2.16 (m, Cy, 12 H), 1.76–1.63 (m 30 H), 1.28–1.24 (s (br), Cy, 18 H), −2.36 (t, Mo–*H*, $^2J_{PH}$ = 25.2 Hz)
	^{31}P{^{1}H}	56.3 (s)
	IR	ν_{CO} = 1912 (vs), 1993 (w); ν_{NO} = 1638 (s)
trans,*trans*-Mo(OTf)(CO)$_2$(NO)(PPh$_3$)$_2$ (**4a**)	^{1}H	7.55–7.53 (m, Ph, 12 H), 7.42–7.40 (m, Ph, 18 H)
	^{31}P{^{1}H}	24.5 (s)
	IR	ν_{CO} = 1963 (vs), 2072 (w); ν_{NO} = 1667 (s); $\nu_{OSO_2CF_3}$ = 1334 (w)
trans,*trans*-Mo(OTf)(CO)$_2$(NO)(PCy$_3$)$_2$ (**4b**)	^{1}H	2.28–2.22 (m, Cy, 6 H), 2.00–1.98 (m, Cy, 12 H), 1.89–1.87 (m 12 H), 1.74 (s (br), Cy, 6 H), 1.59–1.56 (m, Cy, 12 H), 1.35–1.31 (m, Cy, 18 H)
	^{31}P{^{1}H}	41.1 (s)
	IR	ν_{CO} = 1952 (vs), 2036 (w); ν_{NO} = 1656 (s); $\nu_{OSO_2CF_3}$ = 1323 (w)
[*trans*,*trans*-Mo(NH=NPh)(CO)$_2$(NO)(PPh$_3$)$_2$]-[PF$_6$] (**5**)	^{1}H	12.31 (s, 1 H), 7.47 (m, 12 H), 7.45 (m, 2 H), 7.36 (m, 12 H), 7.25 (m, 7 H), 6.89 (d, 2 H); **5**-$^{15}N_2$, 12.31 (dd, $\|^1J_{NH}\|$ = 61.5 Hz, $\|^2J_{NH}\|$ = 3.2 Hz)
	^{31}P{^{1}H}	39.7 (s), −143.4 (sept, PF$_6^-$, $\|^1J_{PF}\|$ = 710 Hz)
	IR	ν_{CO} = 1996 (vs), 2071 (w); ν_{NO} = 1663 (s)
trans,*trans*-Mo(Br)(CO)$_2$(NO)(PPh$_3$)$_2$ (**6**)	^{1}H	7.65–7.62 (m, 12 H, Ph), 7.39–7.31 (m, 18 H, Ph)
	^{31}P{^{1}H}	31.1 (s)
	IR	ν_{CO} = 1962 (vs), 2045 (w); ν_{NO} = 1635 (s)

[a] ^{1}H NMR spectra were recorded at 500 MHz in CDCl$_3$ solution and referenced to residual CHCl$_3$ at δ 7.24; ^{31}P NMR spectra were recorded in CH$_2$Cl$_2$ and were reference to external H$_3$PO$_4$ at δ 0; infrared spectra were recorded as Fluorolube S-30 mulls on CaF$_2$ plates and are given in cm^{-1}.

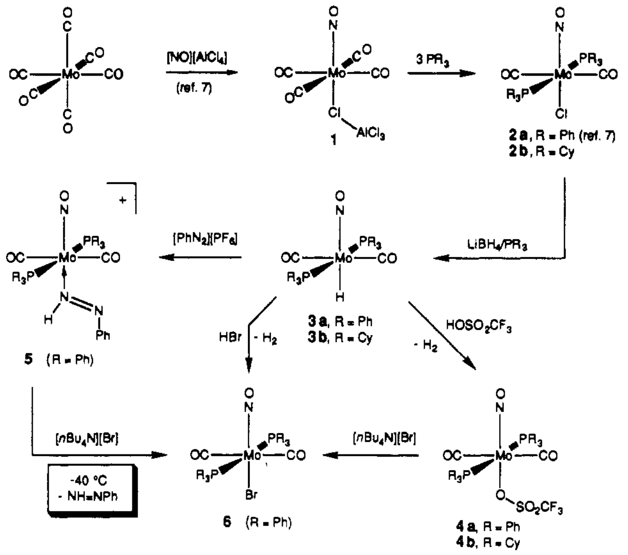
the solids were washed sequentially with ethanol (5 mL) and petroleum ether (10 mL). The product was dried in vacuo to give 145 mg (79% yield). Alternatively, **6** can be prepared by the dropwise addition of aqueous HBr to a methylene chloride solution of **3a**. Anal. Calcd for C$_{38}$H$_{30}$BrNO$_3$P$_2$Mo: C, 58.04; H, 3.84; N, 1.78. Found: C, 57.69; H, 4.01; N, 1.82.

Displacement of ^{15}NH=^{15}NPh from 5-$^{15}N_2$. A 15-mg sample (0.016 mmol) of 5-$^{15}N_2$ and 6 mg (0.02 mmol) of [*n*-Bu$_4$N][Br] were weighed into a sealable 5-mm NMR tube that was attached to a needle valve adapter. The tube was evacuated (10^{-5} Torr), CD$_2$Cl$_2$ (~0.5 mL) was vacuum-transferred into the tube at liquid-nitrogen temperature, and the cold tube was flame-sealed under a dynamic vacuum. The contents of the tube were carefully thawed at −78 °C, and the sample was inserted into the precooled (−40 °C) spectrometer probe. At this temperature the displacement is complete within 60 min, giving **6** (identified by ^{31}P NMR) and the free diazene, ^{15}NH=^{15}NPh (identified by ^{1}H NMR).[4a,8]

Results

The six-coordinate molybdenum chloro complexes *trans*,*trans*-Mo(Cl)(CO)$_2$(NO)(PR$_3$)$_2$ (**2a**, R = Ph; **2b**, R = Cy), prepared by the reaction of 3 equiv of PR$_3$ with *trans*-Mo(ClAlCl$_3$)(NO)(CO)$_4$ (**1**), undergo a metathesis reaction with lithium borohydride in the presence of excess phosphine to afford good yields of the new molybdenum hydrido complexes *trans*,*trans*-Mo(H)(CO)$_2$(NO)(PR$_3$)$_2$ (**3a**, R = Ph; **3b**, R = Cy), as shown in Scheme I. The resonances for the hydride ligands of **3a** and **3b** are observed in the ^{1}H NMR spectra as well-resolved triplets, characteristic of coupling to two equivalent, trans-disposed phosphine ligands ($^2J_{PH}$ ~ 25 Hz), although ν(Mo–H) was not observed in the infrared spectra of the two compounds (see Table I).[9] Protic acids (triflic, hydrobromic) react with the hydrido complexes with evolution of dihydrogen and formation of the conjugate-base adducts *trans*,*trans*-Mo(OTf)(CO)$_2$(NO)(PR$_3$)$_2$ (**4a**, R = Ph; **4b**, R = Cy; OTf = OSO$_2$CF$_3$) and *trans*,*trans*-Mo(Br)(CO)$_2$(NO)(PPh$_3$)$_2$ (**6**). Alternatively, **6** can be prepared by the nucleophilic displacement of the triflato ligand of **4a** by bromide ion.

Scheme I



Similar to the chemistry observed for the known tungsten analogue *trans*,*trans*-W(H)(CO)$_2$(NO)(PPh$_3$)$_2$,[10] benzenediazonium hexafluorophosphate undergoes a clean 1,1-insertion reaction with acetone solutions of the hydrido complex **3a** to give [*trans*,*trans*-Mo(NH=NPh)(CO)$_2$(NO)(PPh$_3$)$_2$][PF$_6$] (**5**) as a red salt in excellent yield (see Scheme I). The signature diazenyl (N*H*) proton resonance appears at δ 12.31 in the ^{1}H NMR spectrum of **5** (CDCl$_3$ solution), and it is split into the expected doublet-of-doublets in **5**-$^{15}N_2$ ($|^1J_{NH}|$ = 61.5 Hz, and $|^2J_{NH}|$ = 3.2 Hz).

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(8) Myers, A. G.; Finney, N. S. *J. Am. Chem. Soc.* **1990**, *112*, 9641.

(9) The infrared spectrum of *trans*,*trans*-Mo(^{2}H)(CO)$_2$(NO)(PPh$_3$)$_2$ exhibits ν(NO) = 1631 cm^{-1}, indicating that the trans nitrosyl and hydride ligands are resonance coupled with a 22-cm^{-1} coupling energy. No ν(Mo–^{2}H) was observed in the expected region at ~1150 cm^{-1}, indicating that this band has very low intrinsic intensity. This is completely analogous to the W derivative, *trans*,*trans*-W(H)(CO)$_2$(NO)(PPh$_3$)$_2$, which has been previously reported.[10]

(10) Hillhouse, G. L.; Haymore, B. L. *Inorg. Chem.* **1987**, *26*, 1876.

Cold methylene chloride solutions of **5** react (−40 °C) with tetrabutylammonium bromide under anaerobic conditions to effect the clean displacement of the coordinated phenyldiazene ligand with formation of the neutral molybdenum bromide complex **6**. The free NH═NPh shows a characteristic diazenyl proton resonance at δ 15.45 (^{1}H NMR; CD_2Cl_2 solution), and the coupling constants ($|^1J_{NH}|$ = 49.4 Hz and $|^2J_{NH}|$ = 2.0 Hz) observed in the free ^{15}NH═^{15}NPh generated from **5**-$^{15}N_2$ are identical to those previously found for phenyldiazene prepared from [W(^{15}NH═^{15}NPh)$(CO)_2(NO)(PPh_3)_2$][PF_6] (at ~0 °C, CD_2Cl_2 solvent)[4a] and are virtually identical to those reported for phenyldiazene prepared from the oxidation of [$^{15}N_2$]phenylhydrazine by 4-methyl-1,2,4-triazoline-3,5-dione (MTAD) in THF-d_8 ($|^1J_{NH}|$ = 51.6 Hz and $|^2J_{NH}|$ = 2.0 Hz).[8] At the temperature of the displacement (−40 °C), there is no noticeable decomposition of NH═NPh to benzene and dinitrogen, as judged by ^{1}H NMR spectroscopy.

Discussion

We have previously demonstrated that coordination complexes of tungsten possessing ligated phenyldiazene (NH═NPh) and methyldiazene (NH═NMe) are useful precursors (via a nucleophilic displacement reaction involving bromide ion) to the free NH═NR molecules.[4] Two observations regarding the diazene displacements from tungsten suggested to us that it might be advantageous to extend this chemistry to include the molybdenum analogues, where the NH═NR ligands would be expected to be more labile. First, the displacement reactions of phenyl- and methyldiazene from [*trans,trans*-W(NH═NR)$(CO)_2(NO)(PPh_3)_2^+$] occur at about 0 °C, and decomposition of NH═NR to N_2 and R–H occurs at a modest (but appreciable) rate at this temperature. Second, although the diazene ligands are coordinated to W in a cis fashion (i.e., H cis to R) as shown by single-crystal X-ray data,[11] the displaced molecules manifest spectroscopic parameters that suggest they have undergone a cis → trans isomerism.[12] It was our hope that a low(er) temperature displacement might afford the opportunity of characterize the *cis*-diazenes before they rearranged to the trans isomers.

The convenient synthetic protocol that provides access to the key hydrido complex *trans,trans*-W(H)$(CO)_2(NO)(PPh_3)_2$ is unfortunately inappropriate for the molybdenum derivative because the action of nitrosonium salts on $Mo(CO)_4(PPh_3)_2$ yields dinitrosyl products instead of the desired mononitrosyl, [*cis,-mer*-$Mo(CO)_3(NO)(PPh_3)_2^+$].[10] However, we have found that *trans,trans*-Mo(H)$(CO)_2(NO)(PPh_3)_2$ (**3a**) can be prepared in good yield by the $LiBH_4$ reduction of *trans,trans*-Mo(Cl)$(CO)_2(NO)(PPh_3)_2$ (**2a**)[7] (see Scheme I). Moreover, this procedure, utilizing isolable *trans*-$Mo(ClAlCl_3)(NO)(CO)_4$ (**1**), has the advantage of being amenable to the trivial incorporation of other phosphines, as demonstrated for the tricyclohexylphosphine complexes *trans,trans*-Mo(Cl)$(CO)_2(NO)(PCy_3)_2$ (**2b**) and *trans,trans*-Mo(H)$(CO)_2(NO)(PCy_3)_2$ (**3b**).

Complexes **3a** and **3b** exhibit characteristic upfield resonances (triplets at δ −1.43 and −2.36, respectively) for the hydride ligands in their ^{1}H NMR spectra ($CDCl_3$ solution), and infrared and ^{31}P NMR data confirm the *trans,trans*-arrangement of the two carbonyl and two phosphine ligands in the complexes. Triflic acid reacts with **3a** and **3b** to give dihydrogen and complexes possessing coordinated triflate ligands, *trans,trans*-Mo(OTf)$(CO)_2(NO)(PR_3)_2$ (**4a**, R = Ph; **4b**, R = Cy), providing chemical evidence supporting the formulation of **3a** and **3b** as molybdenum hydrides. Preliminary experiments suggest that the triflate ligands in **4a** and **4b** can be displaced by a variety of σ-donor ligands, making these compounds useful precursors to a number of new complexes containing the [$Mo(CO)_2(NO)(PR_3)_2^+$] fragment (which is isolobal with the $Mo(CO)_5$ fragment).

Although we have not yet explored the reaction chemistry of these hydrides to the same extent as we have for *trans,trans*-W(H)$(CO)_2(NO)(PPh_3)_2$, it is noteworthy that benzenediazonium hexafluorophosphate undergoes a 1,1-insertion reaction with acetone solutions of **3a** to give the new phenyldiazene complex [*trans,trans*-Mo(NH═NPh)$(CO)_2(NO)(PPh_3)_2$][PF_6] (**5**) as a red salt in excellent yield. The displacement of NH═NPh from **5** by bromide ion was carried out in a sealed NMR tube and monitored by low-temperature ^{1}H NMR spectroscopy. The displacement occurs at about −40 °C over the period of 1 h, and at this temperature, decomposition of NH═NPh (to give N_2 and benzene) is negligible. Thus, as we hoped, this molybdenum-based route seems to be a viable method for generating NH═NPh under conditions amenable to carrying out a proper kinetic investigation of its poorly understood N_2-extrusion process, and we are currently pursuing this.

We had also hoped that the lower temperature displacement of NH═NPh from **5** would allow us to investigate the phenomenon of the cis-to-trans isomerism of phenyldiazene. Unfortunately, even at −40 °C a rapid isomerism about the N═N bond of the free NH═NPh apparently occurs, going from a cis geometry when it is coordinated to the metal to a trans geometry for the free molecule.[11] While we have not spectroscopically detected any other species and the mechanism of this facile isomerism has not been determined, it may well be simply a proton-catalyzed event (i.e., via NH_2═NPh^+). A final comment regarding these geometrical assignments is in order. It is clear from extensive isotopic labeling experiments (specifically, ^{15}N) by Myers[8] and us[4a] that the same, single isomer of NH═NPh is observed under conditions in which the phenyldiazene is generated by very different methods, including our transition-metal-based system in which we have convincing evidence that it is coordinated to the metal center as *cis*-NH═NPh. On the basis of $^1J_{NN}$ coupling,[8] Myers assigns this common isomer as *trans*-NH═NPh (and this seems to be a reasonable conclusion). Such stereochemical assignments made in the absence of the other isomer are inherently tenuous, so it would still be useful to spectroscopically observe the other isomer (probably cis) in order to unambiguously characterize these species.

Conclusions

New hydride and phenyldiazene complexes of molybdenum have been prepared that allow for the clean generation of NH═NPh at −40 °C via a displacement of the coordinated NH═NPh ligand by bromide ion. At this temperature, phenyldiazene is quite stable, so this seems to be a promising route to this and related diazene molecules. Although the synthesis of the key hydrido complex *trans,trans*-Mo(H)$(CO)_2(NO)(PPh_3)_2$ follows a different protocol than that for the tungsten analogue, the reaction chemistries of the Mo and W compounds appear to be very similar.

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(11) We have not been successful in obtaining X-ray-quality crystals of [*trans,trans*-M(NH═NPh)$(CO)_2(NO)(PPh_3)_2^+$] (M = Mo, W) to crystallographically demonstrate that the NH═NPh ligand adopts a cis geometry in these complexes. However, the structure of the methyldiazene complex [*trans,trans*-W(NH═NMe)$(CO)_2(NO)(PPh_3)_2^+$] has been determined and shows cis geometry about the N–N bond, apparently mandated on steric grounds.[4c] When a trans geometry about the N–N bond is artificially imposed (in a CHEMX modeling experiment), *severe* steric interactions are observed between the methyl group and the aryl groups of the PPh_3 ligands. This effect is exacerbated in the phenyldiazene complex; thus, we are confident that the NH═NPh, when ligated, possesses a cis geometry.

(12) We initially assigned the geometries of free NH═NPh and NH═NMe prepared by our displacement reactions as cis, on the basis of (a) small $^2J_{NH}$ values (~2 Hz) and (b) the fact that the diazenes are coordinated to tungsten with cis geometries. We now have several examples of compounds for which this $^2J_{NH}$ coupling criterion for stereochemical assignment about N═N bonds clearly does not hold.[5] Thus, while this seems to be a valid method for assigning geometries in many carbon–nitrogen multiply-bonded systems,[13] it is not a valid method for assigning geometries of diazenes.

(13) (a) Levy, G. C.; Lichter, R. L. *Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy*; Wiley: New York, 1979. (b) Crepaux, D.; Lehn, J. M. *Mol. Phys.* **1968**, *14*, 547. (c) Crepaux, D.; Lehn, J. M. *Mol. Phys.* **1969**, *16*, 225. (d) Yeh, H. J. C.; Ziffer, H.; Jerina, D. M.; Boyd, D. R. *J. Am. Chem. Soc.* **1973**, *95*, 2741. (e) Boyd, D. R.; Watson, C. G.; Jennings, W. B.; Jerina, D. M. *J. Chem. Soc., Chem. Commun.* **1972**, 183.

1538 *Inorg. Chem.* **1992**, *31*, 1538-1540

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Ortho-Metalation of DPPE across a Dirhodium(II,II) Core. Synthesis and X-ray Crystal Structure of $[Rh_2(form)(O_2CCF_3)\{(C_6H_5)_2P(CH_2)_2P(C_6H_5)(C_6H_4)\}(DPPE)]CF_3COO$ (form = *N*,*N*′-Di-*p*-tolylformamidinate Anion, DPPE = 1,2-Bis(diphenylphosphino)ethane)

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The class of coordination compounds containing the Rh_2^{4+} core still represents an attractive field of research due to their many interesting structural, chemical,[1] catalytic,[2] and biochemical properties.[3] While few additional data were reported on the $Rh_2(carboxylate)_4$ systems, there were a number of significant reports on Rh_2^{4+} complexes containing phosphorus donors[4] and especially anionic bidentate nitrogen donors as bridging ligands.[5] The presence of the latter ligands, on the one hand, enhances the metal-based redox processes facilitating the thermodynamic access to mixed-valent species. On the other hand, it makes the dirhodium(II,II) species even more inert toward equatorial substitution and in some cases it prevents axial reactivity too. For example, the complex $Rh_2(form)_4$ (form = *N*,*N*′-di-*p*-tolylformamidinate anion)[5] is inert toward equatorial substitution and shows only poor axial reactivity for steric reasons. On the contrary, the complex $Rh_2(form)_2(O_2CCF_3)_2(H_2O)_2$[6] has a rich chemistry and has proven to be an ideal starting material for the synthesis of other Rh_2^{4+} complexes. Its chemistry is characterized, in addition to an usual axial reactivity, also by a remarkable lability of the trifluoroacetate groups, which leads to mild conditions for the coordination of neutral ligands at the equatorial position. We recently reported conclusive evidence for such behavior synthesizing Rh_2^{4+} complexes containing monodentate (PPh_3, PCy_3)[7] or bidentate neutral ligands (Ph_2PPy)[8] in the equatorial position. In all the reactions performed the Rh-(form)$_2$-Rh fragment remains intact.

As a prelude to detailed investigation of the chemistry of $Rh_2(form)_2(O_2CCF_3)_2(H_2O)_2$ with bidentate phosphorus and nitrogen ligands, we have examined the reactivity of the above complex with dppe. This leads to an unexpected and novel result, namely an ortho-metalation under mild conditions of a diphosphine across a Rh-Rh bond. In this paper we report the synthesis and crystallographic characterization of the complex $[Rh_2(form)(O_2CCF_3)\{(C_6H_4)(C_6H_5)P(CH_2)_2P(C_6H_5)_2\}(dppe)]CF_3COO$ (dppe = 1,2-bis(diphenylphosphino)ethane), which represents the first example of a diphosphine ortho-metalated across a metal-metal bond as well as the first report on a dirhodium(II,II) complex supported by three different bridging ligands.

Table I. Crystallographic Data

formula	$C_{71}H_{63}F_6N_2O_{4.5}P_4Rh_2$	space group	*Pbca*
fw	1460	*T*, °C	23
a, Å	20.578 (4)	λ, Å	0.71073
b, Å	23.808 (4)	ρ_{calcd}, g cm^{-1}	1.52
c, Å	26.078 (4)	μ, cm^{-1}	6.4
V, Å^3	12776.1	R^a	0.049
Z	8	$R_w{}^b$	0.052

[a] $R = [\sum|F_o| - |F_c|]/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = n/(\sigma^2(F_o))$.

Experimental Section

$Rh_2(form)_2(O_2CCF_3)_2(H_2O)_2$ was prepared according to the literature procedure.[6] Other reagents and solvents were used as received. Infrared spectra were recorded on a Perkin-Elmer FT 43 instrument. Elemental analyses were performed by the Microanalytical Laboratory of the Organic Chemistry Institute of Milan and Analitische Laboratorien Malissa and Reuter, Elbach, West Germany.

Synthesis of $[Rh_2(form)(O_2CCF_3)\{(C_6H_4)(C_6H_5)P(CH_2)_2P(C_6H_5)_2\}(dppe)]CF_3COO$. Crude dppe (0.07 g, 0.17 mmol) was added to a stirred solution of $Rh_2(form)_2(O_2CCF_3)_2(H_2O)_2$ (0.081 g, 0.08 mmol) in diethyl ether (20 mL). The solution changed rapidly to a dark-green, red-orange, and again green color and then slowly to a red color. Stirring of the mixture was continued for 4 h whereupon a dark-red precipitate also formed. After the solvent was removed via a syringe, the residue was washed with diethyl ether and crystallized from CH_2Cl_2/heptane. Yield: 67%. Anal. Calcd for $C_{71}H_{62}N_2P_4O_4F_6Rh_2$: C, 58.73; H, 4.37; N, 1.92; P, 8.53; F, 7.84. Found: C, 57.89; H, 4.38; N, 2.06; P, 9.0; F, 8.0. Infrared spectrum (Nujol mull, cm^{-1}): ν(N$\cdots$C$\cdots$N) 1568; $\nu_{asym}(CO_2)$ 1683 (s), 1635 (s). Molar conductivity (Ω^{-1} cm^2 M^{-1}): λ 62 (CH_2Cl_2, 5×10^{-4} M), 121 (CH_3CN, 5×10^{-4} M).

X-ray Data Collection and Structure Refinement. Suitable crystals of the title complex were obtained by slow evaporation of solvent from a $CHCl_3$-heptane solution. Diffraction measurements were made on Siemens R3m/v four-circle diffractometers using graphite-monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation. Accurate unit-cell dimensions and crystal orientation matrices were obtained from least-squares refinement of 25 strong reflections in the range $14° < 2\theta < 28°$. The compound crystallizes in the orthorhombic *Pbca* space group, with parameters as shown in Table I. Lorentz and polarization corrections were applied to the intensity data, but no absorption correction was made due to the low absorption coefficient and the fairly uniform dimensions of the crystal. The structure was solved by using Patterson methods, successive least-squares refinements, and difference Fourier maps. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were added at calculated positions and included in the structure factor calculations with fixed thermal parameters.

Scattering factors for non-hydrogen atoms were taken from ref 9 and for hydrogen atoms from ref 10. Anomalous dispersion corrections for Rh and P atoms were taken from ref 11. Of 12333 measured independent reflections, 5825 having $I > 3\sigma(I)$ were used to refine 508 parameters to final residuals of $R = 0.049$ and $R_w = 0.052$, with $w = 1.00/(\sigma^2(F_o) + 0.001064F_o^2)$, quality-of-fit indicator = 1.401, and the largest peak = 0.79 e Å^{-3}.

All calculations were performed with the SHELX76[12] and PARST[13] sets

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(1) (a) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; John Wiley and Sons: New York, 1982. (b) Felthouse, T. R. *Prog. Inorg. Chem.* **1982**, *29*, 73. (c) Boyar, E. B.; Robinson, S. D. *Coord. Chem. Rev.* **1983**, *50*, 109.

(2) (a) Doyle, M. P.; Bagheri, V.; Wandless, T. S.; Harn, N. K.; Brinker, D. A.; Eagle, C. T.; Loh, K. *J. Am. Chem. Soc.* **1990**, *112*, 1906. (b) Padwa, A.; Frixell, G. E.; Zhi, L. *J. Am. Chem. Soc.* **1990**, *112*, 3100.

(3) (a) Hall, M. L.; Speer, R. J.; Ridggway, N. J. *J. Clin. Hematol. Oncol.* **1980**, *10*, 25. (b) Fimiani, V.; Ainis, T.; Cavallaro, A.; Piraino, P. *J. Chemotherapy* **1990**, *2*, 319.

(4) Cotton, F. A.; Dunbar, K. R.; Verbruggen, M. G. *J. Am. Chem. Soc.* **1987**, *109*, 5497.

(5) Piraino, P.; Bruno, G.; Lo Schiavo, S.; Laschi, F.; Zanello, P. *Inorg. Chem.* **1987**, *26*, 2205 and references therein.

(6) Piraino, P.; Bruno, G.; Tresoldi, G.; Lo Schiavo, S.; Zanello, P. *Inorg. Chem.* **1987**, *26*, 91.

(7) Rotondo, E.; Mann, B. E.; Tresoldi, G.; Piraino, P. *Inorg. Chem.* **1989**, *28*, 3070.

(8) Rotondo, E.; Bruno, G.; Nicolô, F.; Lo Schiavo, S.; Piraino, P. *Inorg. Chem.* **1991**, *30*, 1195.

(9) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *24*, 321.

(10) Stewart, R. F. *J. Chem. Phys.* **1970**, *53*, 3175.

(11) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

0020-1669/92/1331-1538$03.00/0