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NEW MONO-DINITROGEN COMPLEXES OF MOLYBDENUM*

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Abstract—The synthesis is reported of a mono-dinitrogen complex of molybdenum, $Mo(N_2)(triphos)(PMe_2Ph)_2$, where triphos = $PhP(CH_2CH_2PPh_2)_2$, that yields significant yields of ammonia and hydrazine when treated with HCl or HBr in organic solvents. Generally, increasing the temperature increases the combined yield of ammonia and hydrazine.

The bis-dinitrogen complexes of molybdenum (and tungsten) stand out among all the known dinitrogen complexes of transition metals because of the reactivity of coordinated dinitrogen, as exemplified by: (i) alkylation,[2,3(a)] and (ii) protonation.[1,3] This is in dramatic contrast to the general lack of reaction displayed by coordinated dinitrogen in the many mono-dinitrogen complexes of molybdenum.‡ We wish to report one example of an extensive new series of mono-dinitrogen complexes[5] of molybdenum that react with strong acid to form ammonia or ammonia and hydrazine. These complexes contain five group 15 atoms bound to molybdenum. Only one such complex, $Mo(N_2)(PMe_3)_5$, has been reported previously.[6]

EXPERIMENTAL

General procedures

All preparations and reactions were carried out in a dinitrogen atmosphere or *in vacuo*. Compounds were handled using standard inert atmosphere techniques. Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, TN.

Procedures for acid reactions and analyses of ammonia and hydrazine have been detailed previously.[1]

Reagents and materials. All solvents were reagent grade and dried rigorously by heating at reflux over an appropriate drying agent followed by distillation in a dinitrogen atmosphere and saturated with dinitrogen immediately before use by bubbling the gas through the solvent for up to 3 h. Chemicals were purchased from commercial sources and used without purification. $MoCl_3$(triphos) (1) was prepared according to a published procedure.[1]

Spectral studies. IR spectra (4000–200 cm^{-1}) were recorded on a Perkin-Elmer 283 or 1430 spectrophotometer as KBr pellets. $^{31}P-\{^1H\}$ NMR spectra were obtained with a Varian XL-200 spectrometer operating at 80.984 MHz. Chemical shifts (ppm) are referenced to 85% H_3PO_4. Triphos-phosphorus atom assignments are: central—PhP_a; terminal—Ph_2P_b and Ph_2P_c.

Preparation of $Mo(N_2)(triphos)(PMe_2Ph)_2$. In a dry box ($N_2$ atmosphere) a 500 cm^3 Fischer–Porter pressure bottle was charged with a magnetic stir-bar, 3.0 g (4.07 mmol) $MoCl_3$(triphos) and THF (100 cm^3). To this stirred bright yellow suspension was added PMe_2Ph (1.2 cm, 8.43 mmol) by syringe followed by 1% sodium amalgam (0.6 g Na, 26 mmol). Immediately the reaction vessel was sealed (enclosing *ca* 4.2 equiv. of N_2) and transferred to an ice bath before being pressurized to *ca* 75 lb in^{-2} with argon. The reaction was stirred for *ca* 15 h (with reaction reaching room temperature after a few hours). The reaction vessel was transferred to a N_2-filled glove-bag and depressurized. The dark red solution was decanted from the amalgam and filtered through *ca* 1″ celite in a medium-porosity frit. The

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* Reactions of coordinated dinitrogen—XIX. For Part XVIII see Ref. 1.

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‡ A notable exception would be the reaction of $(MeC_6H_5)Mo(PPh_3)_2N_2$ with $[(C_5H_5)Fe(dmpe)(Me_2CO)]BF_4$ to form the {Mo–N_2–Fe} complex.[4]

resultant filtrate was bubbled vigorously with N_2 until the volume of the solvent was reduced to *ca* 35 cm^3 before *ca* 150 cm^3 MeOH was added, while stirring, in 10-cm^3 aliquots to induce precipitation of a bright orange solid. The solid was collected by filtration and washed with MeOH (two 20-cm^3 aliquots) before being dried *in vacuo* (which causes the solid to acquire a dark brown color). Refilling the drying tube with N_2 restores the characteristic bright orange color. The yield of $Mo(N_2)(triphos)(PMe_2Ph)_2$ was 3.0 g (78%). Calc. for $C_{50}H_{55}MoN_2P_5$: C, 64.24; H, 5.93; N, 3.00; P, 16.56%. Found: C, 63.56; H, 5.93; N, 2.87; P, 16.28%. ^{31}P NMR (C_6D_6): 85.91 (dd, $^2J_{P_aP_e} = 101.5$, $^2J_{P_aP_d} = 11.5$, $^2J_{P_aP_b} = {}^2J_{P_aP_c} = 0.0$ Hz, P_a), 66.41 (ddd, $^2J_{P_bP_d} = 93.0$, $^2J_{P_bP_c} \approx 4$, $^2J_{P_bP_e} \approx 18$ Hz, P_b), 58.96 (complex t, $^2J_{P_cP_d} \approx {}^2J_{P_cP_e} \approx 18$ Hz, P_c), 1.41 (ddt, P_d), -3.57 (ddt, P_e). IR (KBr): ν(NN) 1978 cm^{-1}.

Preparation of fac-$Mo(CO)(triphos)(PMe_2Ph)_2$. Orange **2A** (0.15 g) was placed in a round-bottom flask (50 cm^3) and subjected to a high vacuum (*ca* 48 h) in room light. The color gradually darkened to give a very dark brown colored solid by which time the pressure was 5×10^{-6} torr or less. Refilling the flask with CO (1 atm) resulted in a rapid (*ca* 20 min) restoration of a bright orange solid. IR (KBr): ν(CO) 1768 cm^{-1}. ^{31}P NMR (C_6D_6): 84.89 (ddd, $^2J_{P_aP_d} = 84.9$, $^2J_{P_aP_e} = 9.8$, $^2J_{P_aP_b} = 4.9$ Hz, P_a), 73.93 (split dt, $^2J_{P_bP_e} = 74.3$, $^2J_{P_bP_c} = 16.2$, $^2J_{P_bP_d} = 3.1$ Hz, P_b), 40.76 (multiplet, P_c), 0.61 (split dq, $^2J_{P_dP_e} = 19.7$ Hz, P_d), -2.28 (split dt, P_e).

Preparation of $Mo(^{15}N_2)(triphos)(PMe_2Ph)_2$. This complex was made in an analogous manner to the above carbonyl complex. IR (KBr): ν(NN) 1918 cm^{-1}.

RESULTS AND DISCUSSION

Reduction of $MoCl_3$(triphos) in a large excess of dinitrogen (*ca* 13 equiv.) in the presence of 1 equiv. of monodentate phosphine affords a high yield of the corresponding bis-dinitrogen complex [eqn (1)]:[1,7]

$$MoCl_3(triphos) + PR_3 \xrightarrow[THF]{Na\text{–}Hg,\ N_2} Mo(N_2)_2(triphos)(PR_3), \quad (1)$$

where $PR_3 = PPh_3$ or PPh_2Me. However, when $PR_3 = PMe_2Ph$ an oil rather than a solid was obtained.[8] Similar reactions carried out with only a small excess of dinitrogen (*ca* 4 equiv.) and 2 equiv. of PMe_2Ph or 1 equiv. of a bidentate ligand produced an extensive novel series of mono-dinitrogen complexes [eqn (2)]:[5]

$$MoCl_3(triphos) + L_2 \text{ (or 2L)} \xrightarrow[THF]{Na\text{–}Hg,\ N_2} Mo(N_2)(triphos)(L_2), \quad (2)$$

where L = PMe_2Ph (**2A**), $L_2 = Me_2PCH_2PMe_2$ (**2B**), $L_2 = 1,2\text{-}(Me_2As)_2C_6H_4$ (**2C**), $L_2 = Ph_2PCH_2PPh_2$ (**2D**), $L_2 = Ph_2PCH_2CH_2PPh_2$ (**2E**), or $L_2 = 1,1'\text{-}[Ph_2PC_5H_4]_2Fe$ (**2F**).

Complex **2A**, obtained in 78% yield, gave a first-order spectrum in which four of the phosphorus atoms displayed large *trans* coupling constants, including the PMe_2Ph ligands. Previous work[9] with six-coordinate molybdenum(0) complexes containing the triphos ligand have shown that when triphos adopts a meridional configuration, $J_{P_aP_b} = 0$ Hz, whereas when triphos is facial $J_{P_aP_b} > 0$ Hz. The data clearly show that triphos is facial in **2A** and N_2 is *trans* to a terminal triphos-phosphorus atom, P_c. This is in contrast to the bis-dinitrogen complexes in which triphos is meridional.

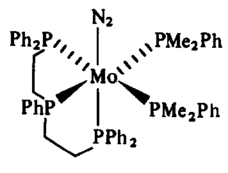

Table 1. Yields of ammonia and hydrazine from $Mo(N_2)(triphos)(PMe_2Ph)_2$ and acid

Acid (mol)	Solvent	Time (h)	Temperature (°C)	N_2[ab]	NH_3[a]	N_2H_4[a]
HCl (40)	CH_2Cl_2	64	18	0.28	0.32	0.17
HBr (40)	CH_2Cl_2	36	18	0.35	0.51	0.30
HCl (36)	Toluene	15	61	0.54	0.51	0.29
HBr (40)	Toluene	39	70	0.56	0.36	0.48
HCl (10)	THF	38	55	—[c]	0.10	0.12
HCl (80)	THF	38	55	0.68	0.84	0.41
HBr (20)	THF	96	25	0.82	0.08	0

[a] Mol (mol of **2A**)$^{-1}$.
[b] Also H_2.
[c] Significant H_2 evolution; total gas = 1.30 mol (mol of **2A**)$^{-1}$.

In vacuo, dinitrogen is slowly lost from solid **2A** to produce a dark brown solid. The process appears to be reversible since exposure of this solid to dinitrogen at room temperature spontaneously regenerates orange **2A**. With $^{15}N_2$ and CO, **2A**-($^{15}N_2$) and $Mo(CO)(triphos)(PMe_2Ph)_2$ are produced, respectively. Reaction of **2A** with CO in solution results in the loss of N_2 and PMe_2Ph.

Complex **2A** reacts with anhydrous HCl and HBr in organic solvents to produce ammonia and hydrazine (see Table 1). Generally, increasing the temperature increases the combined yield of ammonia and hydrazine, as well as producing dihydrogen. As far as we know **2A** is the first mono-dinitrogen complex of any metal that affords significant amounts of ammonia and hydrazine.

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REFERENCES

1. J. A. Baumann, G. E. Bossard, T. A. George, D. B. Howell, L. M. Koczon, R. K. Lester and C. M. Noddings, *Inorg. Chem.* (in press).
2. For example: (a) J. Chatt, R. A. Head, C. J. Leigh and C. J. Pickett, *J. Chem. Soc., Dalton Trans.* 1978, 1638; (b) G. E. Bossard, D. C. Busby, M. Chang, T. A. George and S. D. A. Iske, Jr, *J. Am. Chem. Soc.* 1980, **102**, 1001.
3. For example: (a) J. Chatt, A. A. Diamantis, G. A. Heath, N. E. Hooper and G. J. Leigh, *J. Chem. Soc., Dalton Trans.* 1977, 688; (b) J. Chatt, A. J. Pearman and R. L. Richards, *ibid.* 1977, 1852; (c) T. Takahashi, Y. Mizobe, M. Sato, Y. Uchida and M. Hidai, *J. Am. Chem. Soc.* 1980, **102**, 7461.
4. M. L. H. Green and W. E. Silverthorn, *J. Chem. Soc., Dalton Trans.* 1973, 301.
5. T. A. George and R. C. Tisdale, *J. Am. Chem. Soc.* (in press).
6. (a) M. Brookhardt, K. Cox, F. G. N. Cloke, J. C. Green, M. L. H. Green, P. M. Hare, J. Baskin, A. E. Derome and P. D. Grebenik, *J. Chem. Soc., Dalton Trans.* 1985, 423; (b) F. G. N. Cloke, K. P. Cox, M. L. H. Green, J. Baskin and K. Prout, *J. Chem. Soc., Chem. Commun.* 1982, 393; (c) E. Carmona, J. M. Martin, M. L. Proveda, J. L. Atwood and R. D. Rogers, *J. Am. Chem. Soc.* 1983, **105**, 3014.
7. T. A. George and R. A. Kovar, *Inorg. Chem.* 1981, **20**, 285.
8. R. K. Lester, Ph.D. Thesis, University of Nebraska (1983).
9. M. C. Davies and T. A. George, *J. Organomet. Chem.* 1982, **224**, C25.