J. Am. Chem. Soc. **1982**, *104*, 1537–1548

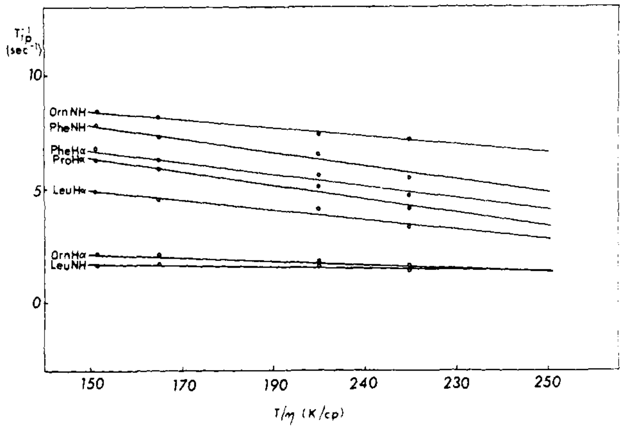


Figure 5. Dependence of R_{1P} ($=1/T_{1P}$) on T/η for the NH and Hα protons of gramicidin S (40 mM in Me_2SO). The temperature was varied from 299 to 329 K.

are the coefficients for self-diffusion of free radical and gramicidin S.

2.3. Correlation of R_{1P} with Temperature Dependence of Amide Chemical Shifts ($\Delta\delta/\Delta T$). $\Delta\delta/\Delta T$ is regarded as one of the best criteria for distinguishing solvent-exposed and solvent-shielded amide protons. R_{1P} appeared to vary linearly with $\Delta\delta/\Delta T$ for Orn^2 NH, Leu^3 NH and D-Phe^4 NH (see Table I).

IV. Conclusions

In general, free radicals increase the relaxation rates of all protons, not just amide protons, in gramicidin S. Protons having greater solvent exposure, and hence access to the unpaired electron of the nitroxide radical, have more enhanced relaxation rates compared to inner protons of the molecule; the latter-include hydrogen-bonded amides, solvent-shielded C Hα's and Orn Hγ's.

The enhancement of spin-lattice relaxation rates R_{1P} was measured as a function of radical concentration and solvent (Me_2SO-d_6 and CD_3OD); R_{1P} vs. concentration curves reflect exposed vs. shielded protons. The paramagnetic relaxation[20,21] theories predict that electron–proton distances in the range 5–20 Å should produce the differential enhancement reported here. We are currently determining ratios of distances and actual distances from the proton relaxation rate enhancements per mole, S_{1P}; these values provide an excellent criterion for evaluating the relative solvent exposure of a proton on a molecule provided no specific nitroxide–molecule complexes exist.

Acknowledgment. This work was supported by the College of Agriculture and Life Sciences of the University of Wisconsin and by Grants AM18604 and PCM7911568 from the National Institutes of Health and National Science Foundation, respectively. Professor W.H. Orme-Johnson is thanked for running the ESR spectra of Tempo solutions. Thanks are due to Mr. Mauro Porcu̇ for his technical assistance.

Registry No. Gramicidin S, 113-73-5; Tempo, 2564-83-2.

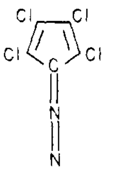
Diazoalkane Complexes of Molybdenum and Tungsten

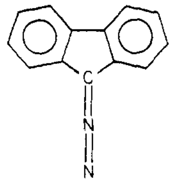
Gregory L. Hillhouse and Barry L. Haymore*

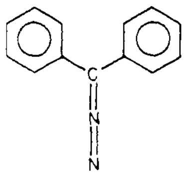
Contribution from the Department of Chemistry, Indiana University,
Bloomington, Indiana 47405. *Received April 22, 1981*

Abstract: Ordinary diazoalkanes, N_2CHR' and $N_2C(CH_3)R'$ ($R' = C_6H_5$, p-$CH_3C_6H_4$), were found to react with $M(CO)_3(S_2CNR_2)_2$ (M = Mo, W; $R = CH_3$, C_2H_5; $R_2 = (CH_2)_4$) at room temperature to form stable complexes of the type $M(CO)(N_2CHR')(S_2CNR_2)_2$ which were conveniently isolated in good yields. Oxidation of $M(CO)(N_2CHR')(S_2CNR_2)_2$ with 1 equiv of Cl_2 or Br_2 produced $MX_2(N_2CHR')(S_2CNR_2)_2$ (X = Cl, Br) which were isolated as chloroform solvates. The addition of excess HBr to $W(CO)(N_2CHR')(S_2CNMe_2)_2$ gave a red solid which analyzed for $WBr_2(N_2H_2CHR')(S_2CNMe_2)_2$. Physical and spectroscopic data suggest that the diazoalkane ligands in the above complexes behave as terminal, singly bent, four-electron donor ligands. The NMR chemical shifts of the methine proton in N_2CHR' ligands indicate that the $M(S_2CNR_2)_2$ unit is strongly electron withdrawing. Syntheses for new tungsten compounds, $W(CO)_3(S_2CNR_2)_2$, $W(CO)_2(S_2CNR_2)_2$, $W(CO)_2(L)(S_2CNR_2)_2$ ($L = p$-$CH_3C_6H_4NHNH_2$, 4-$CH_3C_5H_4N$), $WBr_2(S_2CNR_2)_2$, $W(S_2CNR_2)_4$, and $WBr_3(S_2CNR_2)_2$, are also reported.

Diazoalkanes ($R_2'C{=}N{=}N$) are reactive compounds which find a wide range of synthetic uses as carbene ($R_2'C$:) precursors or as electron-deficient nitrene-like ($R_2'C{=}\ddot{N}$-$\ddot{N}$:) molecules. It is not at all surprising that the interactions of transition-metal complexes with diazoalkanes often lead to the catalytic or stoichiometric evolution of N_2 and the production of free or coordinated carbene reaction products.[1] Indeed, it was not until 1972 that the first isolable mononuclear complexes of diazoalkanes were reported.[2] It is noteworthy that the only published reports of isolable diazoalkane complexes prepared from diazoalkanes and transition metals involve diazoalkanes which are stabilized by strongly electron-withdrawing groups (R′ = –CN, –CF_3, –CO_2R, –C(O)R) or groups which can resonance-stabilize negative charges such as those found in diazotetrachlorocyclopentadiene (A), diazofluorene (B), and diazodiphenylmethane (C).


A


B


C

Interest in diazoalkane complexes not only stems from the plethora of possible new metal-assisted and metal-hindered reactions of the reactive compounds but also from the stereochemistry of the R'_2CNN ligand and its many modes of bonding. A survey of recent chemical literature indicates that at least six

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* To whom correspondence should be addressed at Corporate Research Laboratories, Monsanto Company, St. Louis, MO 63166.

(1) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 800.

(2) Otsuka, S.; Nakamura, A.; Koyama, T.; Tatsuno, Y. *J. Chem. Soc., Chem. Commun.* **1972**, 1105.

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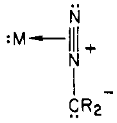
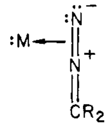
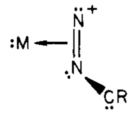
different modes of bonding must be considered. One of the first characterized modes of bonding was the π-bound, two-electron donor R'_2CN_2 ligand (I) which is probably found in complexes $M(CN\text{-}t\text{-}Bu)_2(N_2CR'_2)$ (M = Ni, Pd; R′ = CN, C_6H_5; $R'_2 = C_{12}H_8$), $M(PPh_3)_2(N_2CR'_2)$[2,3] (M = Ni, Pd; R′ = C_6H_5; $R'_2 = C_{12}H_8$), and $(C_5H_5)_2Mo(N_2C_{13}H_8)$.[4] The known structures of $Ni(CN\text{-}t\text{-}Bu)_2(N_2C_{13}H_8)$[5] and $Ru(CO)_2(N_2C_5Cl_4)(PPh_3)_2$[12] contain coordinated diazoalkane ligands best described by a hybrid of formalisms Ib and Ic.

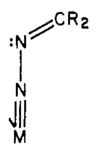

Ia

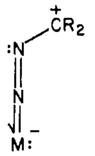

Ib


Ic

The second characterized mode of bonding is the terminal, four-electron donor R'_2CN_2 ligand (II, III) which is probably found in complexes $MX(N_2CR'_2)(diphos)_2^+$ and $MX_2(N_2CR'_2)(PMe_2Ph)_3$ (M = Mo, W; X = F, Cl, Br; R′ = H, CH_3, C_6H_5; diphos = $Ph_2PCH_2CH_2PPh_2$).[6,7] The structures of $WBr(N_2CMe_2)(diphos)_2^+$ and $WF(N_2C(Me)CH_2C(O)CH_3)(diphos)_2^+$ contain coordinated diazoalkane ligands best described by a hybrid of formalisms IIIa and IIIb with IIIa predominating.[8] The formation of the $WBr(N_2CHR'_2)(diphos)_2$ from $WBr(N_2CR'_2)(diphos)_2^+$ and a hydride source suggests that formalism IIIb is also important in these diazoalkane complexes.[7] It is interesting that none of the R'_2CN_2 ligands in this second group of complexes was produced from a free diazoalkane, but rather they were prepared according to eq 1 or 2.


II

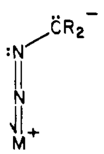

IIIa


IIIb

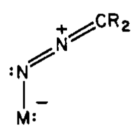
$$W(N_2)_2(diphos)_2 + Me_2CBr_2 \xrightarrow[h\nu]{25\ ^\circ C} [WBr(N_2CMe_2)(diphos)_2][Br] + N_2 \quad (1)$$

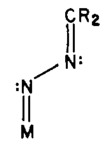
$$MoCl_2(NNH_2)(PMe_2Ph)_3 + PhC(O)Me \xrightarrow{25\ ^\circ C} MoCl_2(N_2CMePh)(PMe_2Ph)_3 + H_2O \quad (2)$$

The third characterized mode of bonding is the terminal, two-electron donor R'_2CN_2 ligand (IV, V, VI, VII) which is probably found in complexes $(C_5H_5)(CO)_3M\text{-}M(C_5H_5)(CO)_2(N_2CHC(O)C_6H_5)$[9] (M = Mo, W), $(C_5H_5)Mn(CO)_2(N_2C(CO_2C_2H_5)_2)$,[10] and $IrCl(N_2CR'_2)(PPh_3)_2$[11,12] (R′ = CF_3; $R'_2C = C_5Cl_4$). The known structures, of $(C_5H_5)Mn(CO)_2(N_2C(CO_2Me)_2)$[10] and $IrCl(N_2C_5Cl_4)(PPh_3)_2$,[12] contain terminally coordinated diazoalkane ligands best described as a hybrid of formalisms IV and V. Complexes in this third group seem to be conveniently characterized by the presence of a strong N–N stretching band in the vibrational spectra in the 1650–2000-cm^{-1} region.[10]

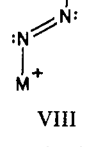

IV


V

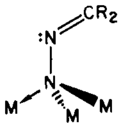

VI

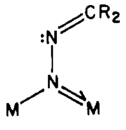

VII

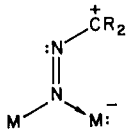
The fourth mode of bonding is the terminal "zero-electron" donor R'_2CN_2 ligand (VIII). No example of this ligand geometry has been structurally characterized; however, vibrational spectral data suggest that such a ligand geometry may be possible for the five-coordinate complexes, $IrCl(N_2C_5Cl_4)(NO)(PPh_3)_2^+$ and $IrCl(N_2C_5Cl_4)(L)(PPh_3)_2$ (L = PMe_3, t-BuNC).[12] A structure like VIII could only be stabilized with a strongly electron-withdrawing group such as tetrachlorocyclopentadiene.

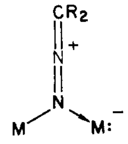

VIII

The remaining modes of bonding involve bridging diazoalkane ligands. The fifth bonding mode is the triply bridging, four-electron donor R'_2CN_2 ligand (IX) which is found in $(C_5H_5)_3Co_3(CO)(N_2C(C_6H_5)_2)$[14] and $Fe_3(CO)_9(N_2C(C_6H_5)_2)_2$;[15] the structure of the iron cluster shows it to have a geometry similar to that depicted by formalism IX with two Fe–Fe bonds.[15] The sixth mode of bonding is the doubly bridging, four-electron donor R'_2CN_2 ligand (X, XI; not all resonance forms depicted) which is found in $(C_5H_5)_2Mo_2(CO)_4(N_2CPh_2)$ whose structure shows the presence of a metal–metal single bond and nearly sp^2 hybridization at the outer (uncoordinated) nitrogen atom.[16] It is


IX


Xa


Xb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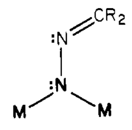
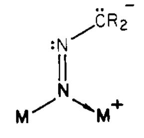

XIIa


XIIb

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[13] In the manganese, molybdenum, and tungsten diazoalkane complexes above, the N–N stretching bands are strongly infrared active. In $IrCl(N_2C_5Cl_4)(PPh_3)_2$ the band is weakly infrared active but strongly Raman active. The absence of an N–N stretching band in the infrared spectrum of $IrCl(N_2C(CF_3)_2)(PPh_3)_2$ does not necessarily indicate a differing mode of coordination for the $N_2C(CF_3)_2$ ligand.

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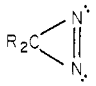
noteworthy that the pentacarbonyl dimer, $(C_5H_5)_2Mo_2(CO)_5(N_2CHR')$,[9] is also known and thought to contain a two-electron donor, terminal diazoalkane ligand. There are as yet no reported examples of a two-electron donor diazoalkane ligand which bridges two metals (XII; not all resonance forms depicted), or of a diazoalkane ligand which has the two nitrogen atoms attached to two different metals.

The electron precise cyclic isomers of diazoalkanes, diazirines, are also known to coordinate to transition metals.



Complexes of diazirines have been prepared,[30] and their properties indicate that the nitrogen ligand acts as a nitrogen σ donor, not unlike ordinary diazenes.

We now report the syntheses and spectroscopic properties of some stable tungsten and molybdenum diazoalkane complexes, $M(CO)(NNCR'_2)(S_2CNR_2)_2$ and $MX_2(NNCR'_2)(S_2CNR_2)_2$ (M = Mo, W; X = Cl, Br), which were prepared in good yield from the respective diazoalkanes. An earlier report erroneously described $W(CO)(N_2CHPh)(S_2CNEt_2)_2$ as $W(CO)(CHPh)(S_2CNEt_2)_2$ and was later corrected.[17]

Experimental Section

Unless otherwise noted, all reactions were carried out at room temperature in freshly distilled solvents under a nitrogen atmosphere using standard Schlenk techniques. Elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, TN., and by Midwest Microlab, Ltd., Indianapolis, IN. The compounds $Mo(CO)(N_2CHTo)(S_2CNMe_2)_2$ and $W(CO)(N_2CHPh)(S_2CNEt_2)_2$ consistently gave low nitrogen analyses when handled in the usual fashion. However, when these complexes (prepared at 25 °C) were kept cold (−20 to −78 °C) until the analyses were performed, excellent, reproducibile results were obtained. Infrared spectra were measured in Fluorolube S-30 and Nujol mulls using a Perkin-Elmer 283 spectrometer and were calibrated by using a polystyrene film. NMR spectra were measured in CD_2Cl_2, $CDCl_3$, or C_6D_6 solution at ambient temperature (unless otherwise noted) using Varian Associates XL-100 (^1H, ^{31}P) and HR-220 (^1H) spectrometers. The spectra were calibrated by using external phosphoric acid (85%) and internal Me_4Si. In some cases, quantitative gas evolution studies were carried out by using Toepler vacuum line techniques to collect the gases and high-resolution mass-spectroscopy to identify and quantify the products (Varian Associates MS-9). Organic products in subsequent reactions were identified by using NMR spectroscopy or a Hewlett-Packard (Model 5992) GC/MS.

Most of the starting materials were prepared by standard techniques. Sodium dithiocarbamate salts were prepared from anhydrous secondary amines, CS_2, and NaOH in absolute EtOH and precipitated by using Et_2O. Thallium dithiocarbamate salts were prepared from the sodium salts and $TlNO_3$ in water or dimethyl sulfoxide; the yellow Tl salts were dried and carefully recrystallized from toluene or p-chlorotoluene; $Mo(CO)_6$ and $W(CO)_6$ were obtained from Pressure Chemical Co., Pittsburgh, PA. Aromatic diazoalkanes were prepared by the method described subsequently which is a convenient modification of Staudinger's original work.[18] While this work was in progress, syntheses for $W(CO)_2(PPh_3)(S_2CNR_2)_2$[19] and $W(CO)_3(S_2CNR_2)_2$[20] appeared in print; our own syntheses, though similar, are given here in detail. Our method for the generation of $W(CO)_3(S_2CNR_2)_2$ avoids the photochemical synthesis of $W(CO)_4I_2$[21] by preparing the bromo analogue[22] which in turn is not isolated as a solid but reacted with dithiocarbamate salts directly in one synthetic step. Both $[Mo(CO)_4Br_2]_2$[22] and $Mo(CO)_3(S_2CNR_2)_2$[23] were prepared by modifications of Colton's original work; $WBr_2(CO)_3(PPh_3)_2$ was prepared by the literature method.[24]

Diazo-p-xylene, $p\text{-}CH_3C_6H_4CHN_2$.[18] In a dropping funnel was placed 20.0 g of p-tolualdehyde which was added slowly to a stirring excess of hydrazine (50 mL of 85% N_2H_4) in a 250-mL round-bottomed flask. After addition was complete (about 30 min), the yellow solution was briefly heated to boiling temperature and then cooled to room temperature. The hydrazone product (ToCH=NNH$_2$) was extracted with two 25-mL portions of dichloromethane. The combined solutions were dried over magnesium sulfate and filtered, and the solvent was removed by using a rotary evaporator. The yield of the p-tolylhydrazone was 18.3 g (83%). The hydrazone was placed in 200 mL of n-pentane, and 40.0 g of yellow mercuric oxide was added to the vigorously stirred mixture. The reaction flask was equipped with a reflux condenser and a cooling bath because the oxidation of the hydrazone was exothermic. The flask was wrapped with aluminum foil to prevent photodecomposition of the product. After being stirred for 2 h under an inert atmosphere, the resulting mixture was briefly dried over magnesium sulfate (magnesium sulfate induced slow decomposition) and quickly filtered through Celite to give a blood-red solution of diazo-p-xylene in pentane.

To retard decomposition of the diazoalkane solution, it was stored as a pentane solution at −78 °C in the dark. Slow decomposition to the corresponding azine (ToCH=NN=CHTo) occurred even under these conditions, so the soloution was warmed to about 0 °C and filtered while cold just prior to usage in order to remove the solid azine which was insoluble in cold pentane. **Diazotoluene** and **1-p-tolyldiazoethane** were prepared similarly. The reaction of hydrazine with 4-methylacetophenone required longer heating times.

Bis(dimethyldithiocarbamato)tricarbonyltungsten(II). Tungsten hexacarbonyl (10.0 g) was suspended in 80 mL of dry CH_2Cl_2 and rapidly stirred in a nitrogen atmosphere at −78 °C (Dry Ice/acetone bath). Dropwise addition of a bromine solution (4.7 g in 10 mL of dry CH_2Cl_2) over a period of 5 min resulted in evolution of carbon monoxide. The mixture was stirred at −78 °C for 10 minutes and then allowed to slowly warm to 0 °C over a period of 20 min after the cold bath was removed. The reaction solution was filtered into another filtered, stirring solution of 20.0 g of $NaS_2CNMe_2{\cdot}2H_2O$ in 200 mL of absolute methanol. The mixture was stirred for 15 min at room temperature to complete the formation of the orange precipitate. The volume of the mixture was reduced by half by using a rotary solvent evaporator, and then the mixture was cooled to −20 °C to ensure more complete crystallization. The mixture was filtered and washed with absolute methanol, then absolute ethanol, and finally pentane. This procedure produced 10.2 g (71%) of a bright orange, microcrystalline powder. **Bis(diethyldithiocarbamato)tricarbonyltungsten** (55% yield) and **bis(tetramethylenedithiocarbamato)tricarbonyltungsten** (66% yield) were prepared analogously.

Bis(dimethyldithiocarbamato)dicarbonyltungsten(II). A 5-g sample of $W(CO)_3(S_2CNMe_2)_2$ was heated in a 150-mL round-bottomed flask under vacuum (0.1 torr) for 3 h at 150 °C by using a hot oil bath. The solid was stirred by using a magnetic stirrer. As the reaction proceeded, the bright orange tricarbonyl converted to the deep green dicarbonyl. The yield was nearly quantitative. The dicarbonyl was very oxygen-sensitive in solution, and even the dry solid completely decomposed on exposure to air after several hours.

Bis(dimethyldithiocarbamato)(4-picoline)dicarbonyltungsten(II). To a solution of 0.18 g of 4-picoline in 25 mL of absolute methanol was added 0.96 g of $W(CO)_2(S_2CNMe_2)_2$. The slurry was stirred at room temperature for 1 h, and the color changed from dark green to dark red-orange. The product was filtered, washed with methanol, and dried under vacuum to yield 0.95 g (83%). **Bis(dimethyldithiocarbamato)(triphenylphosphine)dicarbonyltungsten** (95% yield) and **bis(dimethyldi-**

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thiocarbamato)(*p*-tolylhydrazine)dicarbonyltungsten (81% yield) were prepared analogously. The phosphine complex is stable to air, but the picoline and tolylhydrazine complexes slowly decompose in air.

Bis(dimethyldithiocarbamato)(triphenylphosphine)dicarbonyltungsten(II). A 30-g sample of $WBr_2(CO)_3(PPh_3)_2$ and 22 g of $NaS_2CNMe_2\cdot 2H_2O$ were refluxed for 30 min in a solvent mixture composed of 150 mL of CH_2Cl_2 and 150 mL of CH_3OH. About half the solvent was removed by using a rotary evaporator, and then additional CH_3OH (about 150 mL) was added to the reaction mixture until the volume was the same as that before solvent removal. The mixture was filtered and washed with ethanol and hexane to give red-orange crystals of the 1:1 CH_2Cl_2 solvate which desolvated after several minutes on the filter to give 22.0 g (94%) of solvent-free, orange microcrystalline powder. In applications where traces of Br^- or $Me_2NCS_2^-$ had deleterious effects, the product was carefully recrystallized from CH_2Cl_2/CH_3OH to give a very pure product; total yield after recrystallization was 88%. **Bis(diethyldithiocarbamato)(triphenylphosphine)dicarbonyltungsten** (83% yield) and **bis(tetramethylenedithiocarbamato)(triphenylphosphine)dicarbonyltungsten** (96% yield of 1:1 CH_2Cl_2 solvate) were prepared analogously.

Bis(dimethyldithiocarbamato)carbonyl(diazo-*p*-xylene)tungsten(II). To a stirring solution of 1.00 g of $W(CO)_2(PPh_3)(S_2CNMe_2)_2$ in 10 mL of CH_2Cl_2 was added a freshly prepared solution of diazo-*p*-xylene in *n*-pentane. This dropwise addition of diazo-*p*-xylene resulted in immediate, vigorous evolution of CO and darkening of the solution and was continued until gas evolution ceased. The solution was stirred for 5 min and then reduced in volume under vacuum to 5 mL. Hexane was slowly added to precipitate the brown crystalline solid. The mixture was filtered and washed with *n*-pentane to yield 0.64 g (81%) of the product. An analytical sample was obtained by careful recrystallization from CH_2Cl_2/pentane. When the supernatant solution from the above reaction was evaporated, substantial amounts of the light yellow phosphazine, $Ph_3P{=}NN{=}CHTo$, were recovered contaminated with small amounts of the darker yellow azine, $ToCH{=}NN{=}CHTo$, which resulted from diazoalkane decomposition. When $W(CO)_3(S_2CNMe_2)_2$ was used as the starting material, reaction times and yields were very nearly the same. The following complexes were analogously prepared in the stated yields: **bis(dimethyldithiocarbamato)carbonyl(diazotoluene)tungsten** (91% yield), **bis(dimethyldithiocarbamato)carbonyl(1-*p*-tolyldiazoethane)tungsten** (57% yield), **bis(tetramethylenedithiocarbamato)carbonyl(diazo-*p*-xylene)tungsten** (78% yield), **bis(diethyldithiocarbmato)carbonyl(diazotoluene)tungsten** (73% yield), and **bis(diethyldithiocarbamato)carbonyl(diazo-*p*-xylene)tungsten** (79% yield).

Dibromobis(dimethyldithiocarbamato)(diazo-*p*-xylene)tungsten(IV). A 1.38-g sample of $W(CO)(N_2CHTo)(S_2CNMe_2)_2$ was dissolved in 20 mL of dry CH_2Cl_2 and stirred while 1 equiv (0.38 g in 2 mL of CH_2Cl_2) of Br_2 was added dropwise. Gas evolution was immediate and vigorous. The dark yellow solution was filtered, and the solvent was removed under vacuum at room temperature. The residue was redissolved in 20 mL of $CHCl_3$, and *n*-pentane (200 mL) was added to precipitate 1.42 g (72% yield) of orange-yellow crystals of the 1:1 chloroform solvate. The addition of pentane to the chloroform sometimes produced an oil instead of a solid. Stirring the mixture for 30–60 minutes at room temperature caused the oil to slowly redissolve and deposit yellow microcrystals.

Dichlorobis(dimethyldithiocarbamato)(diazo-*p*-xylene)tungsten(IV). A 1.00-g sample of $W(CO)(N_2CHTo)(S_2CNMe_2)_2$ was dissolved in 30 mL of dry CH_2Cl_2 to give a dark green solution. This solution was visually titrated with a nearly saturated solution of Cl_2 in CH_2Cl_2 to a dark yellow end point. The solvent was removed under vacuum and the residue redissolved in 15 mL of $CHCl_3$. This solution was filtered, and *n*-pentane (200 mL) was added to precipitate the product as yellow crystals of $WCl_2(N_2CHTo)(S_2CNMe_2)_2\cdot CHCl_3$ weighing 0.77 g (60% yield).

Reaction of $W(CO)(N_2CHTo)(S_2CNMe_2)_2$ with Anhydrous HBr. Dry methylene chloride (20 mL) was distilled into an evacuated 100-mL Schlenk flask containing 1.00 g of $W(CO)(N_2CHTo)(S_2CNMe_2)_2$ and a magnetic stirring bar. The solution was placed under an atmosphere of dinitrogen and then hydrogen bromide gas was vigorously bubbled through the stirring solution for about 15 s, causing the color of the solution to change from olive green to deep red. This solution was stirred for 5 min and filtered and the volume of the filtrate reduced under vacuum to 5 mL. Dry pentane (25 mL) was distilled into the flask causing a sticky solid to form. This mixture was vigorously stirred for 1 h, yielding a red powder which was filtered, washed with 50 mL dry pentane, and dried under vacuum to give 0.77 g (63% yield assuming $WBr_2(N_2H_2CHTo)(S_2CNMe_2)_2$).

Tetrakis(dimethyldithiocarbamato)tungsten(IV). (a) A 2-mmol sample of $WBr_2(N_2CHTo)(S_2CNMe_2)_2\cdot CHCl_3$ (1.67 g) and TlS_2CNMe_2 (5 mmol, 1.62 g) were placed in 50 mL of C_6H_6. Gas evolution (N_2) and a color change (yellow to brown) were immediately apparent. The mixture was refluxed for 15 min and cooled, and the volume was reduced to 15 mL. The mixture was filtered, and the solid was dissolved in 50 mL of CH_2Cl_2. This solution was filtered to remove TlBr and other insoluble solids. The volume of the CH_2Cl_2 solution was reduced to about 10 mL, and 80 mL of C_6H_6 was carefully added in order to precipitate the product. This mixture was reduced in volume to about 50 mL and then filtered, and the solid product was dried under vacuum to give 0.74 g (56%) of dark brown crystals. Attempts to use other temperatures (0, 25, 37 °C), other reaction solvents (CH_2Cl_2), or lesser amounts of TlS_2CNMe_2 (2, 1 mmol) all failed to give any other isolable product.

(b) A 1-g sample of $WBr_2(S_2CNMe_2)_2$ and 1.09 g of TlS_2CNMe_2 were refluxed in 500 mL of dry CH_2Cl_2 for 8 h. The cooled mixture was filtered to remove TlBr, and the volume of CH_2Cl_2 was reduced to 25 mL. About 75 mL of C_6H_6 was added, and the volume of the mixture was again reduced to about 25 mL. The mixture was filtered to obtain 0.81 g (71%) of brown crystals.

Bis(dimethyldithiocarbamato)tribromotungsten(V). (a) A solution of 1.20 g of bromine in 2 mL of dry CH_2Cl_2 was added dropwise to a vigorously stirred tungsten solution prepared by dissolving 2.50 g of $W(CO)_3(S_2CNMe_2)_2$ in 25 mL of dry CH_2Cl_2. When gas (CO) evolution ceased (about 10 min), 80 mL of hexane was slowly added to induce precipitation of the product. The mixture was filtered and washed with CH_2Cl_2/hexane (25/75) and then with pure hexane to yield 2.40 g (73%) of glittering black crystals which were dark orange in color when finely pulverized. The product was vacuum dried at room temperature.

(b) A 1-mmol sample (0.58 g) of $WBr_2(S_2CNMe_2)_2$ was suspended in 200 mL of dry CH_2Cl_2 and vigorously stirred. Five drops (18 mg per drop) of Br_2 were added, and an immediate reaction took place which was limited by the solubility of the tungsten dibromide. The mixture was stirred for 1 h, and then its volume was reduced to about 20 mL. Hexane (60 mL) was carefully added to precipitate the black product which was filtered, washed, and dried as before to give 0.55 g (84%).

Bis(dimethyldithiocarbamato)dibromotungsten(IV). (a) A solution of 0.79 g of bromine in 2 mL of dry CH_2Cl_2 was added to 2.50 g of $W(CO)_3(S_2CNMe_2)_2$ in 50 mL of dry CH_2Cl_2. The mixture was refluxed for 3 h, and the green dibromide separated from solution. The mixture was filtered, washed with CH_2Cl_2 and then with hexane, and finally dried under vacuum to give 2.5 g (87%) of a kelly green microcrystalline powder.

(b) Freshly recrystallized samples of $WBr_3(S_2CNMe_2)_2$ (1.33 g) and $W(CO)_3(S_2CNMe_2)_2$ (0.51 g) were dissolved in 50 mL of dry CH_2Cl_2 and then refluxed for 2.5 h. The mixture was filtered, and the nearly insoluble green solid was washed with CH_2Cl_2 and finally hexane. The product was dried under vacuum to yield 1.60 g (91%).

(c) A 2-g sample of $WBr_3(S_2CNMe_2)_2$ was suspended to 50 mL of acetonitrile. The stirring suspension was rapidly heated to reflux. By the time the solvent began to boil, the tribromide had completely dissolved, and almost immediately the green dibromide began to precipitate from solution. After 5 min of refluxing, the cooled reaction mixture was filtered, and the product was washed and dried as before to yield 1.58 g (90%).

(d) Into a solution of 20 mL of dry CH_2Cl_2 and 5 mL of absolute methanol was added 0.50 g of freshly prepared $WBr_2(N_2H_2CHTo)(S_2CNMe_2)_2$. After the mixture was stirred for 1 min, a green precipitate formed which was filtered, washed with 20 mL of methanol and then with 20 mL of CH_2Cl_2, and dried to yield 0.37 g (90%).

Dibromotetracarbonylmolybdenum(II) Dimer. Molybdenum hexacarbonyl (40.0 g) was suspended in 140 mL of dry CH_2Cl_2. The mixture was vigorously stirred and cooled to −78 °C by using a Dry Ice/acetone bath. A nitrogen stream was used to prevent atmospheric moisture and oxygen from entering the reaction flask. Bromine (25.5 g) in 20 mL of dry CH_2Cl_2 was added dropwise over a period of 10 min to the stirring slurry; carbon monoxide evolution commenced immediately. The mixture was stirred for 20 min at low temperature, and then the temperature was slowly increased to 15 °C by removing the cold bath; this warming required 20–30 min. During this time, the reaction went to completion and CO evolution nearly ceased. The reaction mixture was again cooled to −78 °C and stirred for 15 min in order to completely crystallize the product. The mixture was rapidly filtered, washed with pentane, and briefly dried under vacuum (0.1 torr) at room temperature in order to remove residual volatiles. The yield is 49.5 g (89%) of a dense, free-flowing, microcrystalline, orange powder. The product is very sensitive to moisture and slightly sensitive to heat, oxygen and light; it can be indefinitely stored at −20 °C in the dark under a nitrogen atmosphere.

Bis(dimethyldithiocarbamato)tricarbonylmolybdenum(II). To a filtered solution of 14.0 g of $NaS_2CNMe_2\cdot 2H_2O$ in 150 mL of absolute methanol was added a filtered solution of 10.0 g of $[MoBr_2(CO)_4]_2$ in 50 mL of absolute methanol. The reaction mixture was gently stirred during the addition of the molybdenum solution, and carbon monoxide was rapidly evolved. After the solutions were mixed, the mixture was stirred at room temperature for 15 min, and the desired product precipitated from solution. The mixture was filtered, washed twice with absolute ethanol and then pentane to yield 10.8 g (95%) of an orange, microcrystalline powder. The product was contaminated with 5–10% of the burgundy red dicarbonyl, $Mo(CO)_2(S_2CNMe_2)_2$, which resulted from the sppontaneous decarbonylation of the tricarbonyl at room temperature. Under vacuum (0.1 torr), the material could be quantitatively converted (120 °C, 1 h; 30 °C, 8 h) to the dicarbonyl, or under a carbon monoxide atmosphere it could be quantitatively converted to the tricarbonyl. The above tricarbonyl product which was contaminated with small amounts of the dicarbonyl was a suitable starting material for most purposes. This material can be indefinitely stored under an N_2 or CO atmosphere at −20 °C in the dark. The dry solid could be handled in air for brief periods without noticeable decomposition. In the presence of air, $Mo(CO)_3(S_2CNMe_2)_2$ was slowly converted to $MoO(S_2CNMe_2)_2$ and finally to $Mo_2O_3(S_2CNMe_2)_4$. Diethyldithiocarbamate and tetramethylenedithiocarbamate analogues have been prepared analogously.

Bis(dimethyldithiocarbamato)carbonyl(diazo-*p*-xylene)molybdenum(II). This compound was prepared by using the same procedure as the tungsten analogue except that 0.60 g of $Mo(CO)_3(S_2CNMe_2)_2$ was used as the starting material to produce 0.52 g (74% yield) of $Mo(CO)(N_2CHTo)(S_2CNMe_2)_2$ as yellow-brown crystals.

Dibromobis(dimethyldithiocarbamato)(diazo-*p*-xylene)molybdenum(IV). This compound was prepared by using the same procedure as that for $WBr_2(N_2CHTo)(S_2CNMe_2)_2$ except 1.18 g of $Mo(CO)(N_2CHTo)(S_2CNMe_2)_2$ was used to produce 1.19 g (67% yield) of yellow crystals of $MoBr_2(N_2CHTo)(S_2CNMe_2)_2 \cdot CHCl_3$.

Bis(dimethyldithiocarbamato)dibromomolybdenum(IV). (a) The procedure was the same as that for $WBr_3(S_2CNMe_2)_2$ except 2.10 g of $Mo(CO)_3(S_2CNMe_2)_2$ and 0.84 g of Br_2 were used. The yield was 2.29 g (92%) of dark green-black crystals which were olive green in color when finely pulverized. The Mo complex was far more soluble in CH_2Cl_2 and C_6H_6 than the tungsten dibromide analogue. This compound was identical with another sample prepared by other methods.[25]

(b) A solution of 1.00 g of $Mo(CO)(N_2CHTo)(S_2CNMe_2)_2$ in 20 mL of dry CH_2Cl_2 was vigorously stirred under an inert atmosphere, and then anhydrous HBr was vigorously bubbled through the solution for about 30 s; the green solution darkened somewhat. No red color was observed as was the case in the same reaction involving tungsten. The solution was stirred for 10 min and filtered, and the volume of the filtrate reduced under vacuum to about 5 mL. Dry pentane (25 mL) was carefully added causing the dark green product to precipitate. The mixture was filtered, washed with pentane, and dried under vacuum to yield 0.65 g (65%) of the product.

Tetrakis(dimethyldithiocarbamato)molybdenum(IV). A 1-g sample of $MoBr_2(S_2CNMe_2)_2$ and 1.30 g of TlS_2CNMe_2 were refluxed in 50 mL of dry CH_2Cl_2 for 30 min. The cooled solution was filtered to remove the TlBr, and the volume of the remaining solution was reduced to about 20 mL by using a rotary solvent evaporator. A 40-mL sample benzene was then added, and some of the product began to crystallize from solution. The volume of the remaining solution was again reduced to about 15 mL. The mixture was filtered, and the product was dried under vacuum to yield 0.75 g (65%) of brown crystals. The compound was identical with an authentic sample prepared by other methods.[26]

Oxodibromobis(dimethyldithiocarbamato)molybdenum(VI). A 1-g sample of $MoBr_2(S_2CNMe_2)_2$ and 0.35 g of Br_2 were rapidly stirred in 50 mL of CH_2Cl_2 which had 1 mL of H_2O added. This mixture was refluxed for 1 h. The solvent was removed under vacuum, and 20 mL of acetone was added. This mixture was stirred at room temperature for 5 min, filtered, and then washed with acetone and hexane to yield 0.56 g (54%) of a yellow microcrystalline powder. The product was identical with an authentic sample prepared by other methods.[25,27]

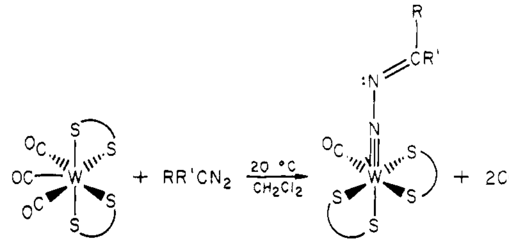
Hydrolysis of $MoBr_2(S_2CNMe_2)_2$. A 1-g sample of $MoBr_2(S_2CNMe_2)_2$ in 40 mL of CH_2Cl_2 and 0.34 g of $NaHCO_3$ in 10 mL of H_2O were mixed and vigorously stirred at room temperature. Great care was taken to maintain an oxygen-free environment. The pink-red CH_2Cl_2 solution was separated from the aqueous phase, dried over anhydrous $MgSO_4$, and separated into two equal portions. One portion was used to measure the UV-visible absorption spectrum and NMR spectrum; these were identical with those measured on an authentic sample of $MoO(S_2CNMe_2)_2$ prepared by different methods.[28] To the second portion was added 0.42 g of $PPhMe_2$. The UV-visible and NMR spectra of the air-sensitive phosphine adduct, $MoO(PPhMe_2)(S_2CNMe_2)_2$, were essentially the same as those measured on an authentic sample (with excess phosphine present) prepared by the action of anhydrous NaS_2CNMe_2 on $MoOCl_2(PPhMe_2)_3$.[29] No attempt was made to isolate the hydrolysis products as solids.

Hydrolysis of $M(CO)(N_2CHTo)(S_2CNMe_2)_2$. (a) Anaerobic. A 0.50-g portion of $Mo(CO)(N_2CHTo)(S_2CNMe_2)_2$ was dissolved in 10 mL of dry CH_2Cl_2 and degassed under vacuum by several freeze–thaw cycles. To this solution was added 1 mL of H_2O which had been similarly degassed, and the mixture was vigorously stirred at reflux under a dinitrogen atmosphere for 6 h. After the mixture was cooled another 5 mL of H_2O was added and the organic phase separated from the aqueous phase. The CH_2Cl_2 solution was dried over $MgSO_4$, filtered, and evaporated to dryness. Analysis of the residue by GC/MS and ^1H NMR spectroscopy indicated the principal organic products to be $ToCH{=}NNH_2$, $ToCH{=}NN{=}CHTo$, and ToCHO with the hydrazone in greatest molar abundance. The IR spectrum of this residue (Nujol mull) showed a strong absorbance at 960 cm^{-1}, indicative of $\nu(MoO)$ for $MoO(S_2CNMe_2)_2$, and no band assignable to $\nu(CO)$ above 1600 cm^{-1}. Also present was a small band at 935 cm^{-1}, assignable to $\nu(MoO)$ in $Mo_2O_3(S_2CNMe_2)_4$. No effort was made to accurately quantify the products. The analogous reaction with tungsten gave similar results; a pure metal-containing product could not be obtained, but infrared bands at 932 and 880 cm^{-1} were indicative of $\nu(WO)$ in $WO_2(S_2CNMe_2)_2$.

(b) Aerobic. A 1.00-g portion of $Mo(CO)(N_2CHTo)(S_2CNMe_2)_2$ was dissolved in 20 mL of CH_2Cl_2 and 2 mL of H_2O was added. The mixture was vigorously stirred in an open flask for 6 h, at which time the products were analyzed as above. The organic products were similar to those found before except that there was more ToCHO than $ToCHNNH_2$; the only molybdenum-containing product was $Mo_2O_3(S_2CNMe_2)_4$ which was isolated in 75% yield.

Results and Discussion

Formation of Diazoalkane Complexes. Ordinary aromatic diazoalkanes, $RR'C{=}N{=}N$ ($R = C_6H_5$, $R' = H$; $R = p\text{-}C_6H_4CH_3$, $R' = H, CH_3$), reacted rapidly with tungsten(II) and molybdenum(II) dithiocarbamate complexes, $M(CO)_3(S_2CNR_2)_2$ ($M = W, Mo$; $R = CH_3, C_2H_5$; $R_2 = (CH_2)_4$), at room temperature in methylene chloride to form dark green mixtures from which nicely crystalline products were obtained in good yields (50–90%).



(3)

Table I contains the physical and spectroscopic properties of these compounds. The same products were produced from similar starting materials such as $M(CO)_2(S_2CNR_2)_2$ and $M(CO)_2(PPh_3)(S_2CNR_2)_2$ ($M = W, Mo$); the reaction times and yields were about the same as analogous reactions with the tricarbonyls. The coordinatively unsaturated dicarbonyl starting materials are more air sensitive and less convenient to use. The dicarbonyl phosphine complexes are convenient starting materials, but 2 equiv of the diazoalkane were required and exactly 1 equiv of the respective phosphazine,[31] $Ph_3P{=}NN{=}CRR'$, was produced as a byproduct (eq 4). The phosphazine byproducts were isolated as

$$M(CO)_2(PPh_3)(S_2CNR_2)_2 + 2RR'CN_2 \rightarrow M(CO)(N_2CRR')(S_2CNR_2)_2 + CO + Ph_3PN_2CRR' \quad (4)$$

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(31) Staudinger, H.; Meyer, J. *Helv. Chim. Acta* **1919**, *2*, 619. $Ph_3P{=}NN{=}CHTo$ is less stable than $Ph_3P{=}NN{=}CPh_2$, but can be isolated in a pure state as pale yellow crystals. ^1H NMR of $Ph_3PNNCHTo$ in $CDCl_3$: δ 2.15 (s, 3 H), 7.45 (m, 19 H), 8.35 (d, 1 H, $^4J_{PH} = 3.5$ Hz). $^{31}P\{^1H\}$ NMR of $Ph_3PNNCHTo$ in CH_2Cl_2: δ 18.95 (s, 1 P). $^{31}P\{^1H\}$ NMR of $Ph_3PNNCHPh$ in CH_2Cl_2: δ 19.55 (s, 1 P).

Table I. Physical and Spectroscopic Properties of W and Mo Complexes

compd,^{a} color	elemental anal. found (calcd)	ν(CO),^{c} cm^{-1}	ν(CN),^{c} cm^{-1}	^{1}H NMR resonances (δ)^e		
				diazoalkane	dithiocarbamate	
$W(CO)(N_2CHTo)(S_2CNMe_2)_2$,^{b} brown	C: 30.59 (30.83) H: 3.59 (3.45) N: 9.33 (9.59)	1920	1530	8.59, 8.55^i (s, H) 7.36, 6.98^i (qt, C_6H_4) 2.30, 1.82^i (s, CH_3)	3.40 (s, 2 × CH_3) 3.30 (s, CH_3) 3.18 (s, CH_3)	2.43^i (s, CH_3) 2.39^i (s, CH_3) 2.34^i (s, CH_3) 2.27^i (s, CH_3)
$W(CO)(N_2CHPh)(S_2CNMe_2)_2$,^{b} brown	C: 29.45 (29.48) H: 3.28 (3.18) N: 9.71 (9.82)	1919	1530	8.64, 8.50^i (s, H) 7.6, 7.0^i (m, C_6H_5)	3.40 (s, 2 × CH_3) 3.30 (s, CH_3) 3.20 (s, CH_3)	2.43^i (s, CH_3) 2.39^i (s, CH_3) 2.35^i (s, CH_3) 2.30^i (s, CH_3)
$W(CO)(N_2CMeTo)(S_2CNMe_2)_2 \cdot CH_2Cl_2$,^{b} dark green	C: 29.94 (29.92) H: 3.66 (3.54) N: 8.47 (8.20)	1919^d	1527	7.42, 7.16^i (qt, C_6H_4) 2.29, 1.89^i (s, $C_6H_4\mathit{CH}_3$) 2.13, 2.00^i (s, CH_3)	3.40 (s, 2 × CH_3) 3.32 (s, CH_3) 3.20 (s, CH_3)	2.45^i (s, CH_3) 2.41^i (s, CH_3) 2.38^i (s, CH_3) 2.32^i (s, CH_3)
$W(CO)(N_2CHTo)(S_2CNEt_2)_2 \cdot CH_2Cl_2$,^{b} dark green	C: 33.51 (33.16) H: 4.36 (4.17) N: 7.91 (7.73)	1922	1498	8.54 (s, H) 7.37 (qt, C_6H_4) 2.27 (s, CH_3)	3.8 (m, 3 × CH_2) 3.57 (a, CH_2) 1.24 (t, CH_3)	1.33 (t, CH_3) 1.35 (t, CH_3) 1.38 (t, CH_3)
$W(CO)(N_2CHPh)(S_2CNEt_2)_2$,^{b} brown	C: 34.60 (34.51) H: 4.10 (4.18) N: 9.17 (8.94)	1923^d	1497	8.57 (s, H) 7.5 (m, C_6H_5)	3.8 (m, 3 × CH_2) 3.52 (a, CH_2) 1.20 (t, CH_3)	1.29 (t, CH_3) 1.31 (t, CH_3) 1.33 (t, CH_3)
$W(CO)(N_2CHTo)(S_2CN(CH_2)_4)_2$,^{b} dark brown	C: 36.13 (35.85) H: 3.98 (3.80) N: 8.59 (8.80)	1920	1494	8.59 (s, H) 7.39 (qt, C_6H_4) 2.30 (s, CH_3)	3.8 (m, 4 × $N\mathit{CH}_2CH_2$) 2.0 (m, 4 × $NCH_2\mathit{CH}_2$)	
$Mo(CO)(N_2CHTo)(S_2CNMe_2)_2$,^{b} yellow-brown	C: 35.80 (36.28) H: 4.04 (4.06) N: 11.58 (11.28)	1955	1524	8.50, 8.30^i (s, H) 7.35, 6.89^i (qt, C_6H_4) 2.33, 1.84^i (s, CH_3)	3.47 (s, 2 × CH_3) 3.38 (s, CH_3) 3.24 (s, CH_3)	2.57^i (s, CH_3) 2.52^i (s, CH_3) 2.50^i (s, CH_3) 2.41^i (s, CH_3)
$WCl_2(N_2CHTo)(S_2CNMe_2)_2 \cdot CHCl_3$, yellow	C: 25.41 (24.13) H: 3.15 (2.83) N: 7.59 (7.50)		1546	9.13 (s, H) 7.41 (qt, C_6H_4) 2.38 (s, CH_3)	3.26 (s, br, 4 × CH_3)	
$WBr_2(N_2CHTo)(S_2CNMe_2)_2 \cdot CHCl_3$, yellow-orange	C: 21.82 (21.56) H: 2.87 (2.53) N: 6.63 (6.70)		1549	9.11 (s, H) 7.43 (qt, C_6H_4) 2.36 (s, CH_3)	3.28 (s, 2 × CH_3) 3.25 (s, 2 × CH_3)	
$MoBr_2(N_2CHTo)(S_2CNMe_2)_2 \cdot CHCl_3$, yellow	C: 24.39 (24.10) H: 2.89 (2.83) N: 7.40 (7.49)		1543	9.07 (s, H) 7.40 (qt, C_6H_4) 2.37 (s, CH_3)	3.37 (s, br, 4 × CH_3)	
$W(CO)_3(S_2CNMe_2)_2$, orange	C: 21.47 (21.27) H: 2.46 (2.37) N: 5.55 (5.51)	1884 1924^d 2018	1529		3.25 (s, 4 × CH_3)	
$W(CO)_3(S_2CNEt_2)_2$, orange	C: 27.17 (27.66) H: 3.50 (3.57) N: 4.84 (4.96)	1886 1928^d 2019	1501		1.30 (t, 4 × CH_3) 3.73 (qt, 4 × CH_2)	
$W(CO)_3(S_2CN(CH_2)_4)_2$, orange	C: 27.81 (27.86) H: 2.99 (2.88) N: 4.79 (5.00)	1887 1927 2018	1499		2.1 (m, 4 × $NCH_2\mathit{CH}_2$) 3.7 (m, 4 × $N\mathit{CH}_2CH_2$)	
$W(CO)_2(4\text{-}NC_5H_4CH_3)(S_2CNMe_2)_2$, orange	C: 29.01 (29.32) H: 3.49 (3.34) N: 7.02 (7.33)	1810 1905	1528	2.37 (s, CH_3)^g 7.22 (d, 2 × CH)^g 8.57 (d, 2 × CH)^g	3.19 (s, 4 × CH_3)	
$W(CO)_2(4\text{-}NH_2NHC_6H_4CH_3)(S_2CNMe_2)_2$, orange	C: 29.66 (29.90) H: 3.60 (3.68) N: 9.00 (9.30)	1803 1899	1528	2.30 (s, CH_3)^g 7.13 (qt, C_6H_4)^g	3.29 (s, 4 × CH_3)	

$W(CO)_2(PPh_3)(S_2CNMe_2)_2$, orange	C: 42.34 (42.05) H: 3.81 (3.66) N: 3.71 (3.77)	1820 1908	1518	7.3 (m, 3 × C_6H_5)[g] 34.35 (s, br, 30 °C, ^{31}P)[g]	3.07 (s, 4 × CH_3)
$W(CO)_2(PPh_3)(S_2CNEt_2)_2$, orange	C: 45.02 (45.11) H: 4.59 (4.42) N: 3.40 (3.51)	1832 1920	1489	7.3 (m, 3 × C_6H_5)[g] 37.77 (s, −80 °C, ^{31}P)[g] $^1J_{PW}$ = 442 Hz	1.18 (t, 4 × CH_3) 3.57 (qt, 4 × CH_2)
$W(CO)_2(PPh_3)(S_2CN(CH_2)_4)_2 \cdot CH_2Cl_2$, red-orange	C: 42.49 (42.38) H: 3.88 (3.79) N: 3.39 (3.19)	1831 1920	1492	7.3 (m, 3 × C_6H_5)[g] 34.23 (s, br, 30 °C, ^{31}P)[g]	1.9 (m, 4 × $NCH_2\mathit{CH}_2$) 3.6 (m, 4 × $N\mathit{CH}_2CH_2$)
$W(CO)_2(S_2CNMe_2)_2$, green	C: 19.71 (20.01) H: 2.45 (2.52) N: 5.69 (5.83)	1802 1934	1546		*f*
$Mo(CO)_3(S_2CNMe_2)_2$, orange	C: 25.50 (25.71) H: 2.99 (2.88) N: 6.78 (6.66)	1898, 1938 2030	1526		3.47 (s, 4 × CH_3)
$Mo(CO)_2(S_2CNMe_2)_2$, magenta	C: 24.59 (24.49) H: 3.27 (3.08) N: 7.09 (7.14)	1838 1928	1536		3.28 (s, 4 × CH_3)
$WBr_3(S_2CNMe_2)_2$, black	C: 10.80 (10.85) H: 1.98 (1.82) N: 4.07 (4.22)		1568		
$WBr_2(S_2CNMe_2)_2$, bright green	C: 12.33 (12.34) H: 2.35 (2.07) N: 4.94 (4.80)		1555		
$W(S_2CNMe_2)_4$, green-brown	C: 21.46 (21.68) H: 3.61 (3.64) N: 8.29 (8.43)		1545		
$MoBr_2(S_2CNMe_2)_2$, olive green	C: 14.19 (14.52) H: 2.70 (2.44) N: 5.59 (5.65)		1545		
$Mo(S_2CNMe_2)_4$, red-brown	C: 25.10 (24.99) H: 4.31 (4.19) N: 9.61 (9.71)		1518		
$WBr_2(N_2H_2CHTo)(S_2CNMe_2)_2$, red	C: 22.89 (23.41) H: 2.97 (3.09) N: 7.31 (7.80) Br: 22.89 (22.25) S: 17.47 (17.86)		1559		
$[MoBr_2(CO)_4]_2$, orange	*f*	1963, 1996, 2050, 2105			

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[a] Abbreviations: Me = CH_3, Et = C_2H_5, Ph = C_6H_5, To = p-$C_6H_4CH_3$. [b] Compounds have a deep green color in solution ($CHCl_3$). [c] Infrared spectra were measured in Fluorolube mulls; ν(CN) is for dithiocarbamate ligand. [d] Sometimes solid state splitting was observed; absent in CH_2Cl_2 solution. [e] Measured at ambient temperature in $CDCl_3$ or CD_2Cl_2 with tetramethylsilane as internal standard; a = AB part of ABX_3, s = singlet, t = triplet, q = quartet, m = multiplet, qt = AA′BB′ quartet, br = broad. [f] Not measured or determined. [g] ^1H resonances for substituted phosphine, hydrazine, or pyridine ligand; $^{31}P\{^1H\}$ resonances for phosphine ligand–external 85% H_3PO_4 reference. [h] See text. [i] In C_6D_6 solvent.

yellow crystalline solids from the reaction mixtures and were quantitatively determined by using ^{31}P NMR spectroscopy.

These new diazoalkane complexes are dark green to brown in color and are stable under ambient atmospheric conditions for short periods (30–90 min) without noticeable decomposition. They can be stored indefinitely under a dinitrogen atmosphere at −20 °C in a dark refrigerator. Exposure of the diazoalkane complexes to dry O_2 at 25 °C in the dark causes partial decomposition after a week with the evolution of small amounts of CO and N_2. The compounds decompose more slowly in the dark under an N_2 atmosphere, but they decompose faster under the influence of moderately intense fluorescent lighting (N_2 atmosphere). The anaerobic decomposition products have not been completely characterized; the gaseous products consist of mostly CO with only small amounts of N_2. Under vacuum (0.1 torr) the decomposition rates were significantly enhanced even to the extent that two of the complexes could not be dried under vacuum.

In addition to the presence of heat, light, reduced pressure, and O_2, water also caused significant decomposition. The reaction of water and $Mo(CO)(N_2CHTo)(S_2CNMe_2)_2$ in CH_2Cl_2 was studied more carefully (eq 5). The primary molybdenum product

$$Mo(CO)(N_2CHTo)(S_2CNMe_2)_2 + H_2O \rightarrow MoO(S_2CNMe_2)_2 + CO + ToCHNNH_2 \quad (5)$$

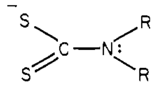
was the molybdenum(IV) oxo complex, $MoO(S_2CNMe_2)_2$, with lesser amounts of $Mo_2O_3(S_2CNMe_2)_4$ which probably formed from the oxidation of Mo(IV) with small amounts of O_2. When the hydrolysis reaction was carried out in air, $Mo_2O_3(S_2CNMe_2)_4$ was the sole isolable product containing Mo. The organic products of the anaerobic hydrolysis consisted primarily of the hydrazone ($ToCH{=}NNH_2$) with lesser amounts of tolualdazine, hydrazine, and tolualdehyde. When air was present, tolualdehyde became the primary hydrolysis byproduct; we have not yet determined whether atmospheric O_2 plays a role in this reaction.

Analogous hydrolysis reactions using $W(CO)(N_2CHTo)(S_2CNMe_2)_2$ produced the same organic products after somewhat longer reaction times. However, no pure tungsten-containing product could be obtained, only a light brown mixture. This material contained (determined by IR and NMR spectroscopy) no carbonyl ligand nor any organic group containing a *p*-tolyl moiety. In addition to the absorptions in the infrared spectrum characteristic of coordinated $Me_2NCS_2^-$, new bands at 932, 880, and 800 (broad) cm^{-1} characteristic of W–O bonding were seen. The first two bands are very similar to those reported for $WO_2(S_2CNMe_2)_2$[32] (934, 889 cm^{-1}), and the broad band at 800 cm^{-1} is similar to that reported for the uncharacterized decomposition product from $WO_2(S_2CNMe_2)_2$. We thus seem to obtain $WO_2(S_2CNMe_2)_2$ from the hydrolysis of the diazoalkane complex. Apart from the adventitious presence of O_2, it is not clear how the anticipated W(IV) product is oxidized to W(VI), but the presence of $WO_2(S_2CNMe_2)_2$ is not at all surprising in light of the high stability of tungsten(VI) oxo complexes relative to lower valent tungsten oxo complexes,[32] especially when an oxygen source (H_2O) in present.

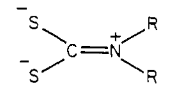
It seems likely that the hydrolysis reactions of both Mo and W complexes, $M(CO)(N_2CR'_2)(S_2CNR_2)_2$, initially follow the same course. The effects of heat, light, reduced pressure, O_2, and H_2O on $M(CO)(N_2CR'_2)(S_2CNR_2)_2$ suggest that the important first step in its reaction and/or decomposition is carbonyl loss which is then followed by subsequent reaction steps (eq 6). The

$$M(CO)(N_2CR'_2)(S_2CNR_2)_2 \xrightarrow{-CO} M(N_2CR'_2)(S_2CNR_2)_2 \rightarrow \text{further reaction} \quad (6)$$

ready synthesis and stability of similar five-coordinate, 16-electron complexes, $MoO(S_2CNR_2)_2$[28] and $ReN(S_2CNEt_2)_2$,[28] lends credibility to such a carbonyl loss. $MoO(S_2CNR_2)_2$ will not add CO but will add other two-electron donor ligands (L) such as acetylenes[33] (HC_2H) and basic phosphines[29] ($PPhMe_2$) forming *cis*-$MoOL(S_2CNR_2)_2$.[34] Attempts to isolate $M(N_2CR'_2)(S_2CNR_2)_2$ have been unsuccessful. It should be noted that the action of a large excess of diazoalkane on the green complexes $M(CO)(N_2CR'_2)(S_2CNMe_2)_2$, for longer periods (2 h) produced deep red products in solution with no CO bands in the infrared spectra. Although attempts to isolate pure products such as $M(CR'_2)(N_2CR'_2)(S_2CNMe_2)_2$ or $M(N_2CR'_2)_2(S_2CNMe_2)_2$ have been unsuccessful so far, NMR spectra of the reaction mixtures are not inconsistent with the formation of one of these products. Finally, it should be added that decomposition and hydrolysis rates of the diazoalkane complexes are dependent on the metal and organic groups on the dithiocarbamate ligands. The rates of decomposition under similar conditions follow these sequences: $W(CO)(N_2CR'_2)(S_2CNMe_2)_2 < Mo(CO)(N_2CR'_2)(S_2CNMe_2)_2$ and $W(CO)(N_2CR'_2)(S_2CNMe_2)_2 < W(CO)(N_2CR'_2)(S_2CNEt_2)_2$. Nearly pure solutions of $Mo(CO)(N_2CHTo)(S_2CNEt_2)_2$ in CH_2Cl_2 could be prepared in the usual way, but analyses of the isolated solid always indicated partial decomposition. The decomposition rates are *not* sensitive to the nature of the aromatic diazoalkane used, at least for the limited group of diazoalkanes which were used. Tungsten complexes are known to dissociate CO ligands less readily than Mo analogues, and S_2CNMe_2 ligands inhibit CO dissociation relative to S_2CNEt_2 ligands because the dimethyldithiocarbamate donates more electron density to the metal; hence, ν(CO) is lower and CO loss is retarded through increased M → CO π donation. As compared to the diethyl analogue, the S_2CNMe_2 ligand has a higher value of ν(CN) which correlates well with the above observations and suggests that formalism XIIIb is relatively more important.



XIIIa



XIIIb

A comment about relative reaction rates is in order although detailed kinetic measurements have not been carried out. Simple substitution reactions involving $W(CO)_3(S_2CNMe_2)_2$ and simple σ-donating ligands such as To_3P, $ToNHNH_2$, or 4-picoline require at least several hours to complete (25 °C, CH_2Cl_2) and are at least 1–2 orders of magnitude slower than substitution reactions involving $W(CO)_3(S_2CNMe_2)_2$ and diazoalkanes or other π-bonding nitrogen ligands such as ToN_2^+, ToN_3, and NO^+ which have Lewis acid behavior. On the other hand, the addition of phosphines, hydrazines, and pyridines to $W(CO)_2(S_2CNMe_2)_2$ is complete on mixing and prior dissociation of CO from the tricarbonyl is implicated as one important mechanistic pathway (eq 7 and 8).

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[32] Chen, G. J.; McDonald, S. W.; Newton, W. E. *Inorg. Chim. Acta* **1976**, *10*, L67.

[33] Maatta, E. A.; Wentworth, R. A. D.; Newton, W. E.; McDonald, J. W.; Watt, G. D. *J. Am. Chem. Soc.* **1978**, *100*, 1320.

[34] With the assumption that a four-electron donor terminal $R_2C{=}\ddot{N}{-}\ddot{N}{:}$ ligand has a negligible trans influence like a four-electron donor terminal $R_2\ddot{N}{-}\ddot{N}{:}$ ligand or $R{-}\ddot{N}{:}$ ligand, then the initial ligand addition reaction (eq A) to $MoO(S_2CNR_2)_2$ should be disfavored when compared to the same addition reaction to $Mo(N_2CR'_2)(S_2CNR_2)_2$ because the oxo ligand exerts a significant trans influence.

$$\underset{\substack{\text{square pyramid}\\ \text{axial oxygen}}}{MoO(S_2CNR_2)_2} + L \underset{A}{\rightleftharpoons} trans\text{-}MoOL(S_2CNR_2)_2 \underset{B}{\rightleftharpoons} cis\text{-}MoOL(S_2CNR_2)_2$$

[35] For example, $(C_5H_5)_2WH(NNHPh)^+$ and $ReCl_2(NH_3)(NNHPh)(PMe_2Ph)_2^+$: Carroll, J. A.; Sutton, D.; Cowie, M.; Gauthier, M. D., *J. Chem. Soc., Chem. Commun.* **1979**, 1058. Douglas, P. G.; Galbraith, A. R.; Shaw, B. L. *Transition Met. Chem. (N.Y.)* **1975**, *1*, 17.

[36] For example, $(C_5H_5)Mn(CO)_2(NH{=}NPh)$ and $ReCl(CO)_2(HN{=}NPh)(PPh_3)_2$: Sellmann, D.; Weiss, W. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 880. Haymore, B. L., unpublished results.

[37] For example, $(C_5H_5)Mn(CO)_2(C{=}CHPh)$: Nesmeyanov, A. N.; Aleksandrov, G. G.; Antonova, A. B.; Anisimov, K. N.; Kolobova, N. E.; Struchkov, Y. T. *J. Organomet. Chem.* **1976**, *110*, C36.

[38] For example, $(C_5H_5)Mn(CO)_2(HC{\equiv}CPh)$: Strohmeier, W.; Hellmann, H. *Chem. Ber.* **1965**, 98, 1598.

[39] For example, $(CO)_5W(C(OH)Ph)$: Fischer, E. O.; Kreis, G.; Kreissl, F. R. *J. Organomet. Chem.* **1973** *56*, C37.

[40] Bestmann, H. J.; Fouad, M. S.; Geibel, K. *J. Organomet. Chem.* **1980**, *192*, 177.

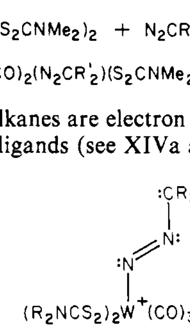
$$W(CO)_3(S_2CNMe_2)_2 \rightleftharpoons W(CO)_2(S_2CNMe_2)_2 + CO \quad (7)$$

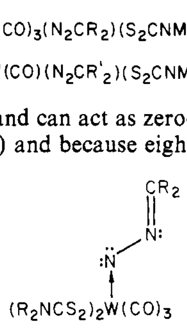
$$W(CO)_2(S_2CNMe_2)_2 + L \rightarrow W(CO)_2L(S_2CNMe_2)_2 \quad (8)$$

Certainly the much faster substitution of CO by diazoalkanes must follow a different, probably associative, pathway (eq 9). Because

$$W(CO)_3(S_2CNMe_2)_2 + N_2CR'_2 \longrightarrow W(CO)_3(N_2CR_2)(S_2CNMe_2)_2 \xrightarrow{-CO} W(CO)_2(N_2CR'_2)(S_2CNMe_2)_2 \underset{-CO}{\rightleftharpoons} W(CO)(N_2CR'_2)(S_2CNMe_2)_2 \quad (9)$$

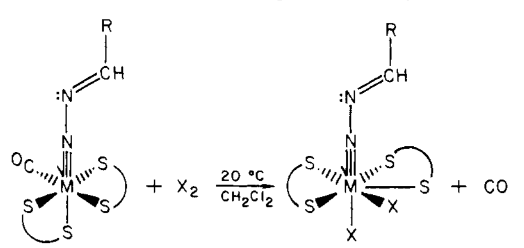
diazoalkanes are electron deficient and can act as zero-electron donor ligands (see XIVa and XIVb) and because eight-coordination is not unreasonable for W, especially with sterically small dithiocarbamate ligands (cf. $W(S_2CNMe_2)_4$), simple addition of the diazoalkane to the tricarbonyl followed by successive CO dissociations with concomitant electronic and geometric changes (zero-electron donor → two-electron donor → four-electron donor) in the attached diazoalkane is a possible mechanistic pathway for CO substitution.


XIVa


XIVb

The reaction of $W(CO)_3(S_2CNR_2)_2$ with ToN_3 proceeds more slowly than that with the isoelectronic $ToCHN_2$ but still much faster than the reactions with PPh_3, $ToNHNH_2$, etc.; furthermore, the final product from the azide reaction, $W(CO)(NTo)(S_2CNR_2)_2$,[17] has lost a dinitrogen molecule. Why the difference? It is likely that both the tolyldiazoalkane and tolyl azide interact with the tungsten tricarbonyl in the same way. Indeed, a rapidly formed and easily detected (but difficult to isolate) yellow intermediate is present in the azide reactions.[17] This may well be the azide complex, $W(CO)(N_3To)(S_2CNMe_2)_2$, which subsequently loses N_2 to form $W(CO)(NTo)(S_2CNR_2)_2$. The N_2 loss is undoubtedly thermodynamically favorable and one four-electron nitrogen donor (azide, N_3R) is replaced by another four-electron nitrogen donor (nitrene, NR). However, if $W(CO)(N_2CHR')(S_2CNR_2)_2$ loses N_2, the four-electron nitrogen donor (diazoalkane) is replaced by a two-electron carbon donor (carbene). In addition, the lone pair on the outer nitrogen atom (attached to the organic group) in $W{\equiv}N{-}\ddot{N}{=}\ddot{N}{-}R$ may well facilitate the decomposition of the RN_3 complex because this lone pair is available for bonding to its own or another tungsten atom.

The addition of 1 equiv of chlorine or bromine to $M(CO)(N_2CR'_2)(S_2CNR_2)_2$ proceeds smoothly and rapidly at room temperature in methylene chloride to form $MX_2(N_2CR'_2)(S_2CNR_2)_2$ and CO (eq 10). The yellow to orange


(10)

X = Cl, Br

products can be isolated in good yield as the 1:1 chloroform solvates from chloroform/pentane mixtures. Excess halogen has deleterious effects on the yields and purity of the products. Bromine is conveniently weighed out, but not chlorine. However, the nearly instantaneous and sharp color change (deep green to yellow-orange) allows one to add just enough halogen solution (CH_2Cl_2) to effect the complete color change. Repeated efforts to prepare $M(N_2CR'_2)(S_2CNR_2)_3^+$ from $MX_2(N_2CR'_2)(S_2CNR_2)_2$ and NaS_2CNR_2 or TlS_2CNR_2 in acetone, benzene, or methylene chloride failed; instead, reasonable yields of $W(S_2CNMe_2)_4$ were obtained. The analogous molybdenum reactions produced $Mo(S_2CNR_2)_4$ which, however, was not easily separated from other byproducts (eq 11). Even when a deficiency

$$WX_2(N_2CR'_2)(S_2CNR_2)_2 + 2TlS_2CNR_2 \rightarrow W(S_2CNR_2)_4 + N_2 + 2TlX \quad (11)$$

of dithiocarbamate (0.5–1.0 equiv/metal) was used in reaction 11, the only isolable product was the same compound. Stoichiometric amounts of dinitrogen were evolved in the reactions, but the fate of the remainder of the diazoalkane ligand was not determined. The addition of diazoalkanes to $MBr_2(S_2CNMe_2)_2$ (M = Mo, W) resulted in vigorous reactions but no $MBr_2(N_2CR'_2)(S_2CNMe_2)_2$ was produced; these reactions are being studied further.

The proton NMR spectra (Table I) give some insight into the geometries of the diazoalkane complexes. The presence of three singlet resonances in the ratio 1:1:2 for the dithiocarbamate ligands of $W(CO)(N_2CHTo)(S_2CNMe_2)_2$ and related complexes in $CDCl_3$ solution suggests a rigid cis, pseudooctahedral geometry on the NMR time scale. At low temperature (−60 °C) and high field (220 MHz), the resonance corresponding to two methyl groups does not split into two signals. Although one dithiocarbamate ligand might be rotating about the C–N multiple bond, we thought that this was unlikely and that the two methyl resonances were accidently degenerate. We confirmed this by using C_6D_6 solutions at 220 MHz; the spectra displayed four equally intense methyl singlets for the two dithiocarbamate ligands. The ^1H NMR spectrum of $W(CO)(N_2CHTo)(S_2CNEt_2)_2$ in $CDCl_3$ has four equally intense 1:2:1 triplets for the four CH_3 groups and a complicated multiplet consisting of four overlapping AB signals (from four ABX_3 patterns) for the four CH_2 groups. The only other six-coordinate geometry which is consistent with four inequivalent methyl or ethyl groups on the dithiocarbamate ligands is a trigonal-prismatic geometry with three sulfur atoms on one trigonal face; for steric reasons, we consider this geometry unlikely. The geometry of the seven-coordinate diazoalkane complexes is a little less certain. The presence of two singlet resonances in the ratio of 2:2 for the dithiocarbamate ligands in $WBr_2(N_2CHTo)(S_2CNMe_2)_2$ does not uniquely define a coordination geometry. However, on the basis of the known pentagonal-bipyramidal geometry of $MoCl_2(NPh)(S_2CNEt_2)_2$ (axial Cl, NPh), we believe that the seven-coordinate diazoalkane complexes have similar pentagonal-bipyramidal geometries (axial halogen, diazoalkane);[41] the NMR spectra are at least consistent with such a suggestion. The geometries of the starting materials, $M(CO)_3(S_2CNR_2)_2$, $M(CO)_2(PR'_3)(S_2CNR_2)_2$, and $M(CO)_2(S_2CNR_2)_2$, are known.[20]

The NMR chemical shift of the methine proton of the monosubstituted diazomethane ligand ($RC\mathit{H}N_2$) seems to give some indication of the effect of the metal on the coordinated diazoalkane. The resonances of the methine protons in the phosphine diazoalkane complexes are found in the region δ 5.5–6.0, only 1 ppm downfield from the free diazoalkanes while the methine protons in the dithiocarbomate diazoalkane complexes are found 4 ppm downfield from the free diazoalkanes. The diazoalkane complexes can be described by resonance structures IIIa and IIIb. The NMR data indicate that the contribution of IIIa is greater in the dithiocarbamate complexes than in the phosphine complexes because the dithiocarbamate ligands promote stronger metal–diazoalkane π bonding. These observations are consistent with known chemical properties: (1) $W(CO)_3(S_2CNMe_2)_2$ and $W(CO)_2(S_2CNMe_2)_2$ have lower C–O stretching frequencies in their infrared spectra than do $WX_2(CO)_3(PPh_3)_2$ and $WX_2(CO)_2(PPh_3)_2$ (X = Cl, Br), and $W(CO)_3(S_2CNMe_2)_2$ decarbonylates with greater difficulty than $WX_2(CO)_3(PPh_3)_2$; (2) the diazoalkane ligand in $WX(N_2CHPh)(diphos)_2^+$ is attacked by H^-, but the diazoalkane ligand in $W(CO)(N_2CHPh)(S_2CNMe_2)_2$ is attacked by H^+ apparently at a different site (vide infra).

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[41] Maatta, E. A.; Haymore, B. L.; Wentworth, R. A. D. *Inorg. Chem.* **1980**, *19*, 1055.

Table II. Chemical Shifts of Methine Protons

compd	chem shift ($CDCl_3$), ppm	compd	chem shift ($CDCl_3$), ppm
PhCH=O	10.0	$PhCH{=}N{-}N{\equiv}WBr_2(S_2CNMe_2)_2$	9.1
PhCH=N–N=CHPh	8.6	$PhCH{=}N{-}N{\equiv}MoBr_2(S_2CNMe_2)_2$	9.1
PhCH=NPh	8.4	$PhCH{=}N{-}N{\equiv}W(CO)(S_2CNMe_2)_2$	8.6
$PhC(O)CH{=}N{-}N{=}PPh_3$[40]	8.3	$PhCH{=}N{-}N{\equiv}Mo(CO)(S_2CNMe_2)_2$	8.5
$PhCH{=}N{-}N{=}PPh_3$	8.2	$PhCH{=}N{-}N{\equiv}WBr(diphos)_2{}^+Br^-$ (CD_2Cl_2)[7]	6.1
$PhCH{=}N{-}NH{-}C_6H_4NO_2$	7.8	$PhCH{=}N{-}N{\equiv}WF(diphos)_2{}^+BF_4{}^-$ (CD_2Cl_2)[8]	5.8
$PhCH{=}N{-}NH_2$	7.4	$PhCH{=}N{-}N{\equiv}MoF(diphos)_2{}^+BF_4{}^-$ (CD_2Cl_2)[8]	5.6
PhCH=N=N(cyclopentane)	4.8	$MeCH{=}N{-}N{\equiv}WBr(diphos)_2{}^+Br^-$ (CD_2Cl_2)[7]	5.5
		$EtCH{=}N{-}N{\equiv}MoF(diphos)_2{}^+BF_4{}^-$ (CD_2Cl_2)[8]	5.4

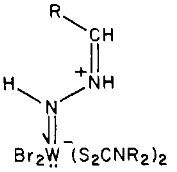
The infrared spectra of the diazoalkane complexes were not unusual. The ν(CN) absorption of the dithiocarbamate ligands followed the expected trends; the absorption was higher for dimethyldithiocarbamate than for the diethyldithiocarbamate analogues. The absorption was higher for tungsten complexes than for molybdenum analogues. The higher formal oxidation state or effective charge on the metal corresponded to a higher value of ν(CN). When strong σ-donating ligands replaced carbonyls, the values of ν(CN) decreased. An interesting comparison is the value of ν(CN) for $WBr_2(S_2CNMe_2)_2$ (1555 cm^{-1}) with those of $WBr_2(N_2CHTo)(S_2CNMe_2)_2$ (1545 cm^{-1}) and $WBr_2(N_2H_2CHTo)(S_2CNMe_2)_2$ (1559 cm^{-1}). However, the replacement of two carbonyl ligands by one diazoalkane ligand in $W(CO)_3(S_2CNR_2)_2$ caused little change in ν(CN). Another interesting result is the low values of ν(CO) for $W(CO)_2(S_2CNMe_2)_2$ at 1802 and 1934 cm^{-1} (1868 cm^{-1} average) and the large carbonyl coupling energy of 132 cm^{-1}; the presence of an empty π orbital in a trigonal-prismatic environment on the metal is probably responsible. Consistent with the proposed geometry (IIIa) for these diazoalkane ligands, no high energy (>1700-cm^{-1}) band, corresponding to the strong 2200-cm^{-1} band in the free diazoalkanes, was observed in the infrared spectra of the complexes. Attempts to identify bands assignable to C=N stretching vibration in the coordinated diazoalkane were frustrated by interferences from the dithiocarbamate ligands.

Reactions with HBr. The addition of a large excess of anhydrous HBr to $W(CO)(N_2CHTo)(S_2CNMe_2)_2$ in methylene chloride at room temperature proceeded rapidly with quantitative liberation of carbon monoxide. From the deep red solutions were obtained dark red crystalline solids upon the addition of pentane. Although the elemental analyses (C, H, N, S, Br) were similar to those for the bromine addition product, $WBr_2(N_2CHTo)(S_2CNMe_2)_2$, the product behaved much differently in solution, and we believe the product to be $WBr_2(N_2H_2CHTo)(S_2CNMe_2)_2$. If only a moderate excess of HBr were used, the red solution gradually (10–15 min) turned green, and a green solid precipitated from solution. Reaction solvents were important. Pure C_6H_6 and CH_2Cl_2 worked well, but C_4H_8O (THF) and CH_3CN caused rapid formation of the green product with the momentary appearance of the red color. The use of damp C_6H_6 or CH_2Cl_2 or the addition of alcohols to the red solutions in C_6H_6 or CH_2Cl_2 caused the conversion of the red to the green product. When the pure, soluble red product was dissolved in *any* pure solvent, the red solution rapidly deposited green crystals within minutes. The only way of preserving the red product in solution was by using HBr saturated $CHCl_3$, CH_2Cl_2, or C_6H_6. If the HBr concentrations were not high enough or if a more basic solvent were used, the red product decomposed in solution. In the solid state, it is stable if kept dry. The nearly insoluble green product was shown to be pure $WBr_2(S_2CNMe_2)_2$ and the primary organic byproduct under nearly acid-free conditions was the respective hydrazone, $ToCH{=}NNH_2$ (eq 12 and 13). The composition of the red HBr reaction product is consistent with the formulation $WBr_2(N_2H_2CHTo)(S_2CNMe_2)_2$ which differs by only two hydrogen atoms from the respective diazoalkane complex prepared by bromine addition. The red complex, which was formed under strongly acidic conditions, is stable only in strongly acidic solutions. Because carbon monoxide is lost during the initial reaction, lower acid concentrations *do not* simply reverse the reaction and cause deprotonation but rather induce the formation of $WBr_2(S_2CNMe_2)_2$. The reaction of anhydrous HBr with the molybdenum complex $Mo(CO)(N_2CHTo)(S_2CNMe_2)_2$ seems to follow a similar course. The red intermediate is not observed and $MoBr_2(S_2CNMe_2)_2$ is immediately formed under all experimental conditions which we employed.

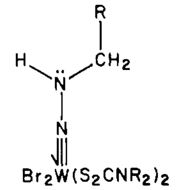
$$W(CO)(N_2CHTo)(S_2CNMe_2)_2 + HBr\ (excess) \xrightarrow[CH_2Cl_2]{20\ ^\circ C} WBr_2(N_2H_2CHTo)(S_2CNMe_2)_2 + CO \quad (12)$$

$$WBr_2(N_2H_2CHTo)(S_2CNMe_2)_2 \xrightarrow[CHCl_3]{20\ ^\circ C} WBr_2(S_2CNMe_2)_2 + ToCH{=}NNH_2 \quad (13)$$

The locations of the two extra hydrogen atoms in $WBr_2(N_2H_2CHTo)(S_2CNMe_2)_2$ have not been determined with certainty. The ^{1}H NMR spectra in CD_2Cl_2 solution (HBr saturated) do not show resonances due to these two protons. The addition of either Bu_4NBr or HSO_3CF_3 to CH_2Cl_2 solutions of $W(CO)(N_2CHTo)(S_2CNMe_2)_2$ indicates that the diazoalkane complex is inert to Br$^-$ but readily attacked by H$^+$. No products could be isolated from the HSO_3CF_3 reactions, but a mixture of Bu_4NBr and HSO_3CF_3 gave red solutions identical with those obtained from HBr. It seems that $WBr_2(N_2H_2CHTo)(S_2CNMe_2)_2$ arises from a series of addition reactions, first by H$^+$ and then Br$^-$, so that 2 equiv of HBr are ultimately added and 1 equiv of carbon monoxide is displaced. On the basis of the known chemistry of $MABr_2(S_2CNR_2)_2$ (M = Mo, W; A = four-electron donor ligand), formalism XV (isohydrazone)



XV



XVI

represents a likely structure; however, we cannot rule out an isodiazene structure like formalism XVI. Both ligands are four-electron π donors. It is noteworthy that $WBr_2(S_2CNMe_2)_2$ and $MoBr_2(S_2CNMe_2)_2$ exist as stable isolable compounds. Despite their apparent coordinative unsaturation, these compounds will not attach themselves to ordinary two-electron donor ligands such as CO, PPh_3, CH_3CN, or C_5H_5N, even when the ligands are present in great abundance. Likewise, attempts to attach tolylhydrazine or tolualdehyde hydrazone to $WBr_2(S_2CNMe_2)_2$ failed. The tetravalent $WBr_2(S_2CNMe_2)_2$ and its molybdenum analogue have no affinity for ordinary nitrogen σ-donor ligands. Thus, it seems that in the absence of strong acid, the four-electron donor N_2H_2CHTo ligand in $WBr_2(N_2H_2CHTo)(S_2CNMe_2)_2$ rearranges to an ordinary two-electron donor hydrazone ligand ($H_2NNCHTo$) which in turn dissociates from the tungsten forming the stable dibromide $WBr_2(S_2CNMe_2)_2$. The stabilization by transition metals of related unstable forms of stable molecules is not without precedent. Transition metals can stabilize isodiazene (aminonitrene, hydrazido(2–)) ligands[35] ($RH\ddot{N}{-}\ddot{N}{:}$) as well as ordinary diazenes[36] ($R\ddot{N}{=}\ddot{N}H$); they can stabilize vinylidene ligands[37] (RCH=C:) as well as ordinary acetylenes[38] (RC≡CH);

they can stabilize hydroxycarbene groups[39] ($\mathrm{R\ddot{C}\underset{..}{\ddot{O}}H}$) in preference to ordinary aldehydes ($\mathrm{RCH{=}\ddot{O}{:}}$) depending on the requirements of the metal. Alkylating agents such as CH_3I, $CH_3OSO_2CF_3$, and $(CH_3)_3O^+$ react with $W(CO)(N_2CHTo)(S_2CNMe_2)_2$, but pure products have not been isolated as yet. Similarly, NO^+, $ToN_2{}^+$, ToN_3, or PMe_2Ph nearly quantitatively displaces CO from $W(CO)(N_2CHTo)(S_2CNMe_2)_2$, but no pure, isolable, metal-containing product has yet been obtained.

Other Reaction of $M(CO)_3(S_2CNR_2)_2$. Although the syntheses of $Mo(CO)_3(S_2CNR_2)_2$[23] and $Mo(CO)_2(S_2CNR_2)_2$[23] have been known for some years, the preparations of the tungsten analogues are new. It seems unusual that the tungsten compounds were not prepared earlier because nearly the same technique that produced the Mo complexes works for the W analogues (eq 14 and 15).

$$\mathrm{W(CO)_6 + Br_2 \xrightarrow[CH_2Cl_2]{-78\ ^\circ C} {}^1/_2[WBr_2(CO)_4]_2 + 2CO} \qquad (14)$$

$$\mathrm{{}^1/_2[WBr_2(CO)_4]_2 + 2NaS_2CNR_2 \xrightarrow[CH_3OH]{25\ ^\circ C} W(CO)_3(S_2CNR_2)_2 + 2NaBr + CO} \qquad (15)$$

The only difference is that $[WBr_2(CO)_4]_2$ is not so easily isolated, so we generated it in situ and used it directly. Both the molybdenum and tungsten tricarbonyl complexes are bright orange in color. The tricarbonyl complexes lose one equivalent of CO to form the coordinatively unsaturated dicarbonyl complexes (eq 16);

$$\mathrm{W(CO)_3(S_2CNR_2)_2 \xrightarrow[vacuum]{150\ ^\circ C} W(CO)_2(S_2CNR_2)_2 + CO} \qquad (16)$$

the Mo dicarbonyl is magenta, but the W dicarbonyl is deep green in color. As expected, the molybdenum tricarbonyl loses CO more readily than the W analogue. In the absence of a CO atmosphere, it is not easy to obtain the molybdenum tricarbonyl completely free of the dicarbonyl owing to partial decarbonylation even at room temperature, but the tungsten tricarbonyl must be heated under vacuum to completely remove 1 equiv of CO. $W(CO)_2(S_2CNR_2)_2$ is quite oxygen sensitive; solutions react rapidly with air, and even the dry solid decomposes after several hours in air. The pure oxidation products were not isolated, but the loss of the two carbonyl bands in the infrared spectra of the light brown oxidation product and the appearance of the two W–O bands characteristic of $WO_2(S_2CNR_2)_2$ suggest that a W(II) to W(VI) oxidation in air took place. If oxygen is carefully excluded, $W(CO)_2(S_2CNR_2)_2$ will take on a variety of σ-donor ligands (L) (eq 17). The reactions are nearly instantaneous at 25 °C and give good yields of monomeric, orange, seven-coordinate products.

$$\mathrm{W(CO)_2(S_2CNR_2)_2 + L \rightarrow W(CO)_2L(S_2CNR_2)_2} \qquad (17)$$

$$\mathrm{L = PPh_3,\ CO,\ 4\text{-}picoline,\ ToNHNH_2}$$

The tungsten(II) and molybdenum(II) tricarbonyls are oxidized by Br_2 in CH_2Cl_2 at room temperature (eq 18 and 19). The

$$\mathrm{Mo(CO)_3(S_2CNMe_2)_2 + Br_2 \xrightarrow[CH_2Cl_2]{20\ ^\circ C} MoBr_2(S_2CNMe_2)_2} \qquad (18)$$

$$\mathrm{W(CO)_3(S_2CNMe_2)_2 + {}^3/_2Br_2 \xrightarrow[CH_2Cl_2]{20\ ^\circ C} WBr_3(S_2CNMe_2)_2} \qquad (19)$$

molybdenum carbonyl gives the known olive green molybdenum(IV) dibromide[25] which is soluble in methylene chloride. The tungsten tricarbonyl consumes more bromine (as judged by CO evolution) to give the brown-black tungsten(V) tribromide $WBr_3(S_2CNMe_2)_2$, which is also soluble in methylene chloride. The green tungsten(IV) dibromide was conveniently made by reducing the tungsten(V) tribromide using warm acetonitrile or 0.5 equivalent of the tungsten(II) tricarbonyl (eq 20–22). In contrast to the Mo analogue, $WBr_2(S_2CNMe_2)_2$ is only slightly soluble in CH_2Cl_2 and almost insoluble in all other ordinary solvents. Notwithstanding, it can be recrystallized by Soxhlet extraction by using CH_2Cl_2. Furthermore, the addition of bromine to the tungsten(IV) dibromide rapidly gave the tungsten(V) tribromide. This explains why the bromine oxidation of $W(CO)_3(S_2CNMe_2)_2$ gave mostly $WBr_3(S_2CNMe_2)_2$. If exactly 1 equiv of Br_2 is added to $W(CO)_3(S_2CNMe_2)_2$, a W(II)–W(V) mixture is obtained which, if allowed to react longer, will give pure W(IV). As noted earlier, all efforts to attach ordinary nitrogen donor ligands (amines, pyridines, hydrazines) to $MBr_2(S_2CNMe_2)_2$ failed to give anything other than starting materials. In order to verify their compositions, the Mo(IV) and W(IV) dibromides were allowed to react with thallous dimethyldithiocarbamate to form the tetrakis(dithiocarbamate) complexes (eq 23).[26] $MoBr_2(S_2CNMe_2)_2$ also was allowed to react with HOBr (Br_2/H_2O) to give the known yellow complex $MoOBr_2(S_2CNMe_2)_2$ (eq 24).[27] In the absence of water, Br_2 did not readily react with $MoBr_2(S_2CNMe_2)_2$.

$$\mathrm{2WBr_3(S_2CNMe_2)_2 + W(CO)_3(S_2CNMe_2)_2 \xrightarrow[CH_2Cl_2]{37\ ^\circ C} 3WBr_2(S_2CNMe_2)_2 + 3CO} \qquad (20)$$

$$\mathrm{WBr_3(S_2CNMe_2)_2 \xrightarrow[CH_3CN]{80\ ^\circ C} WBr_2(S_2CNMe_2)_2} \qquad (21)$$

$$\mathrm{WBr_2(S_2CNMe_2)_2 + {}^1/_2Br_2 \xrightarrow[CH_2Cl_2]{20\ ^\circ C} WBr_3(S_2CNMe_2)_2} \qquad (22)$$

$$\mathrm{MoBr_2(S_2CNMe_2)_2 + 2TlS_2CNMe_2 \xrightarrow[CH_2Cl_2]{37\ ^\circ C} Mo(S_2CNMe_2)_4 + 2TlBr} \qquad (23)$$

$$\mathrm{MoBr_2(S_2CNMe_2)_2 + Br_2 + H_2O \xrightarrow[CH_2Cl_2]{37\ ^\circ C} MoOBr_2(S_2CNMe_2)_2 + 2HBr} \qquad (24)$$

Conclusions. We have shown that thermally stable transition-metal complexes containing ordinary aromatic diazoalkanes as ligands can be readily prepared in good yield starting with the free diazoalkanes. The complexes are unique because (1) they *do not* contain strongly stabilizing, electron-withdrawing groups (R′) on the diazoalkane (R'_2CN_2) such as previously reported diazoalkane complexes where $R' = CF_3$, CN, C(O)R, and CO_2R or $R'_2C = C_{13}H_8$ and C_5Cl_4, (2) they are sufficiently stable to hinder N_2 extrusion in most cases, and (3) they are prepared from the free diazoalkane rather than from precursors such as isodiazene or dinitrogen complexes. While the coordinated diazoalkane is rendered more thermally stable by the metal toward known modes of thermal decomposition (e.g., azine formation), the complexes are quite reactive and are good starting materials for other reactions. Preliminary work shows that these complexes are photochemically active at 0 °C and thermally active above 50 °C in inert solvents. We have also shown that a metal-assisted reduction of diazoalkanes leads to a product which seems to contain an "isohydrazone" ligand. Furthermore, we have shown that the diazoalkane, as a ligand, has strongly amphoteric character with a wide variety of bonding modes and that the organic substituents on the coordinated diazoalkane strongly affect its stability, coordination geometry, and reactivity. It is likely that many more "unstabilized" diazoalkane complexes will be found and that they will lead to a body of chemistry rich in new reactions.

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Registry No. $W(CO)(N_2CHTo)(S_2CNMe_2)_2$, 80664-89-7; $W(CO)(N_2CHPh)(S_2CNMe_2)_2$, 80664-88-6; $W(CO)(N_2CMeTo)(S_2CNMe_2)_2$, 80664-87-5; $W(CO)(N_2CHTo)(S_2CNEt_2)_2$, 80664-86-4; $W(CO)(N_2CHPh)(S_2CNEt_2)_2$, 80664-85-3; $W(CO)(N_2CHTo)(S_2CN(CH_2)_4)_2$, 80664-84-2; $Mo(CO)(N_2CHTo)(S_2CNMe_2)_2$, 80664-90-0; $WCl_2(N_2CHTo)(S_2CNMe_2)_2$, 80664-83-1; $WBr_2(N_2CHTo)(S_2CNMe_2)_2$, 80664-82-0; $MoBr_2(N_2CHTo)(S_2CNMe_2)_2$, 80664-81-9; $W(CO)_3(S_2CNMe_2)_2$, 72881-01-7; $W(CO)_3(S_2CNEt_2)_2$, 72827-54-4; $W(CO)_3(S_2CN(CH_2)_4)_2$, 80664-80-8; $W(CO)_2(4\text{-}NC_5H_4CH_3)(S_2CNMe_2)_2$, 80664-79-5; $W(CO)_2(4\text{-}NH_2NHC_6H_4CH_3)(S_2CNMe_2)_2$, 80664-78-4; $W(CO)_2(PPh_3)(S_2CNMe_2)_2$, 60911-44-6; $W(CO)_2(PPh_3)(S_2CNEt_2)_2$, 60911-45-7; $W(CO)_2(PPh_3)(S_2CN(CH_2)_4)_2$, 80594-71-4; $W(CO)_2(S_2CNMe_2)_2$, 69916-43-4; $Mo(CO)_3(S_2CNMe_2)_2$, 20692-80-2; $Mo(CO)_2(S_2CNMe_2)_2$, 80664-77-3; $WBr_3(S_2CNMe_2)_2$, 80664-76-2; $WBr_2(S_2CNMe_2)_2$, 80664-75-1; $W(S_2CNMe_2)_4$, 61069-37-2; $MoBr_2(S_2CNMe_2)_2$, 80664-74-0; $Mo(S_2CNMe_2)_4$, 33850-23-6; $WBr_2(N_2H_2CHTo)(S_2CNMe_2)_2$, 80664-

73-9; $[MoBr_2(CO)_4]_2$, 80594-72-5; $Mo(CO)_3(S_2CNEt_2)_2$, 18866-21-2; $Mo(CO)_3(S_2CN(CH_2)_4)_2$, 80664-72-8; $WBr_2(N_2CHPh)(S_2CNMe_2)_2$, 80664-71-7; $MoBr_2(N_2CHPh)(S_2CNMe_2)$, 80664-70-6; $Mo(CO)(N_2CHPh)(S_2CNMe_2)_2$, 80664-69-3; $MoOBr_2(S_2CNMe_2)_2$, 57146-53-9; PhCH=O, 100-52-7; PhCH=N—N=CHPh, 588-68-1; PhCH=NPh, 538-51-2; $PhCH{=}N{-}N{=}PPh_3$, 1103-87-3; $PhCH{=}N{-}NH{-}C_6H_4NO_2$, 3078-09-9; $PhCH{=}N{-}NH_2$, 5281-18-5; PhCH=NΔbdN, 766-91-6; $WBr_2(CO)_3(PPh_3)_2$, 18130-07-9; $p\text{-}CH_3C_6H_4CHN_2$, 23304-24-7; $ToCH{=}NNH_2$, 52693-87-5; *p*-tolualdehyde, 104-87-0; 1-*p*-tolydiazoethane, 64252-52-4; 4-methylacetophenone, 122-00-9; tungsten hexacarbonyl, 14040-11-0; molybdenum hexacarbonyl, 13939-06-5.

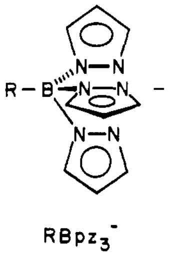
Covalently Bound Paramagnetic Shift Reagents. 1. A Versatile Lithium Reagent Derived from Bis[(4-bromophenyl)tris(1-pyrazolyl)borato]cobalt(II)

David L. White and J. W. Faller*

Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut 06520. *Received March 27, 1981*

Abstract: A versatile precursor for the attachment of covalently bound paramagnetic probes has been prepared. Sodium (4-bromophenyl)tris(1-pyrazolyl)borate, $4\text{-}BrC_6H_4B(pz)_3Na$, was converted to the 4-lithio derivative via a metal–halogen exchange with butyllithium in THF at −70 °C. Deuteration of this lithium reagent could be effected by treatment with D_2O; carbonation, however, led to decomposition. Conversion of $(4\text{-}BrC_6H_4B(pz)_3)_2Co^{II}$ to the corresponding 4-lithio compound followed by deuteration, coupling with 1-iodobutane, or carbonation gave $(4\text{-}RC_6H_4B(pz)_3)_2Co^{II}$, with R = D, *n*-Bu, or CO_2H, respectively. The latter compound was converted to the methyl ester by reaction with diazomethane. The large isotropic shifts observed for protons on the phenyl ring and its substituents can be accurately predicted by using conventional expressions for the dipolar shift.

Hydrotris(1-pyrazolyl)borate, I, and its alkyl and aryl analogues



$RBpz_3^-$

I, R = H
II, R = C_6H_5
III, R = $4\text{-}BrC_6H_5$
IV, R = $4\text{-}LiC_6H_5$

constitute a class of unique uninegative tridentate ligands possessing C_{3v} symmetry. Trofimenko[1] has reported the preparation of a number of these compounds and their complexes with alkaline-earth and transition-metal ions. However, the emphasis heretofore has been on the physical properties of the coordinated metal ions rather than the chemistry of the ligand or the potential applications of the complexes. The kinetic stability and the high symmetry of tris(1-pyrazolyl)borate transition-metal chelates should make this ligand an attractive choice for attaching metal ion probes to drug molecules, proteins, etc., so that their binding to substrates could be investigated. In particular, the very large isotropic shifts of NMR resonances associated with paramagnetic Co(II) in a pseudooctahedral environment with axial symmetry[2] should constitute a powerful probe for the detailed geometry of such complexes. Accordingly, we have synthesized the Na^+ and Co^{2+} complexes of (4-bromophenyl)tris(1-pyrazolyl)borate and studied the formation and reactions of the lithium reagents derived from them. The synthesis of the ligand itself involved a modification of one of the procedures originally described by Trofimenko.[3,4]

Experimental Section

General Comments. Reactions involving lithium reagents were carried out in flame-dried glassware under an atmosphere of prepurified nitrogen. THF and ether were distilled under nitrogen from sodium benzophenone ketyl. Organic reagents were purchased from Aldrich or Eastman Organic Chemicals and used without further purification. *n*-BuLi in hexane solution and NaH in mineral oil dispersion were purchased from Alfa. NMR spectra were recorded on a JEOL FX90-Q 90-MHz or a Bruker 270-MHz spectrometer. Chemical shifts are given in parts per million from internal Me_4Si or DSS with resonances downfield of the reference being positive. IR spectra were recorded on a Beckman IR-4250. HPLC was carried out on a C-8 reversed phase column with 80% CH_3CN–20% aqueous phase (1% aqueous NH_4OAc adjusted to pH 8.5 with concentrated aqueous ammonia). Elemental analyses were performed by Midwest Microlab, Ltd., Indianapolis, IN, or Atlantic Microlab Inc., Atlanta, GA.

$C_6H_5B(pz)_3Na$ (3). A 250-mL round-bottom flask equipped with mechanical stirrer, thermometer, and 20-cm Vigreaux column topped with a distilling head was charged with 16 g (0.24 mol) of pyrazole and 100 mL of diglyme. To this solution at 120 °C was added dropwise over 30 min a solution of 4.9 g (0.04 mol) of $PhB(OH)_2$ in 50 mL of 10% aqueous acetone. Acetone and water were removed from the reaction mixture by fractional distillation until the head temperature reached the boiling point of diglyme (161 °C). The reaction mixture then was cooled to 50 °C and treated portionwise with 3.0 g of 50% NaH dispersion in mineral oil (0.06 mol of NaH). After the foaming had subsided, the mixture was again heated and diglyme was removed by distillation. This required ca. 45 min, and the pot temperature was not allowed to exceed 220 °C. The pot residue solidified upon cooling to room temperature under nitrogen. It was treated with filter aid and 50 mL of water, and the resulting suspension was filtered. Water was removed from the filtrate in vacuo at room temperature. The residue was first triturated with ether and then with hexane to yield 3.7 g of finely divided white powder containing 69% by weight of $PhB(pz)_3Na$ (20% of theory). (The product was assayed by reaction of an aliquot with 0.5 M $CoCl_2$ in 1 M acetate buffer at pH 5.5, extraction with CH_2Cl_2, and HPLC determination of $(PhB(pz)_3)Co$ in the extract.) The ether washes and other residues contained an additional 7% of product.

$4\text{-}BrC_6H_4B(pz)_3Na$. This compound was prepared as above from $4\text{-}BrPhB(OH)_2$. The crude product was 68% pure, and the yield was

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(4) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 3170–3177.

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