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Reactions of Coordinated Dinitrogen. 5.[1] Reactions of Ethyl Haloacetates with Bis(dinitrogen)bis[1,2-bis(diphenylphosphino)ethane]molybdenum[2]

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Bis(dinitrogen)bis[1,2-bis(diphenylphosphino)ethane]molybdenum, $Mo(N_2)_2(dppe)_2$ (**1**), where dppe = $Ph_2PCH_2CH_2PPh_2$, reacts with ethyl haloacetates to form ((ethoxycarbonyl)methyl)diazenido complexes of molybdenum, $MoX(N_2R)(dppe)_2$, where X = Cl, Br, or I and R = $CH_2COOC_2H_5$. Protonation with fluoroboric acid produces the corresponding hydrazides $[MoX(N_2HR)(dppe)_2]BF_4$ where the site of protonation is unambiguously established in solution as the carbon-bound nitrogen atom. For comparison, the diazenide and hydrazide derived from the reaction of **1** with ethyl 3-iodoproprionate have been prepared. The effect of the change in coordinated halogen atom and electron-withdrawing ester group on the infrared and ^{1}H NMR spectra will be discussed.

Introduction

Recently, a number of reports have appeared in the literature concerning the preparation of alkyldiazenido complexes of molybdenum.[1,3] However, except for a preliminary communication of the work to be reported here,[4] only one other example of an organic functionally substituted alkyldiazenido complex of molybdenum has been published.[5] This example is a (tetrahydrofuran-2-yl)diazenide, $MoBr(NNCHOCH_2CH_2CH_2)(dppe)_2$.

Reactions of functionally substituted alkyl halides that form alkyldiazenides are interesting because (a) they enable a study of the tolerance of the general alkyl halide reactions with $Mo(N_2)_2(dppe)_2$ (eq 1; X = Br or I) to the presence of

$$Mo(N_2)_2(dppe)_2 + RX \rightarrow MoX(N_2R)(dppe)_2 + N_2 \qquad (1)$$

functional groups on the organic moiety, (b) the chemical and physical effects of the substituent on the properties of the diazenido group can be investigated, and (c) they have provided a method of preparing alkyldiazenido complexes from alkyl chlorides, something that was not possible previously.[4] However, it is possible to prepare the chlorides by a metathesis reaction with the corresponding bromides or iodides, e.g., eq 2 (X = Br or I; Y = Cl, N_3, NCS, or OH), that have been synthesized by reaction of an alkyl bromide or iodide with **1**.[1,3]

$$MoX(N_2R)(dppe)_2 + Y^- \rightarrow MoY(N_2R)(dppe)_2 + X^- \qquad (2)$$

Experimental Section

All preparations and crystallizations were carried out under a dinitrogen atmosphere by using standard inert atmosphere techniques. Organic solvents were reagent grade and were dried by distillation from the drying agent indicated: benzene, heptane, and dichloromethane (calcium hydride), tetrahydrofuran (sodium benzophenone ketyl or calcium hydride), and methanol (magnesium methoxide). All solvents were deoxygenated before use by bubbling dinitrogen through them for at least 0.5 h, and then the reaction solutions were further deoxygenated by a series of freeze–thaw cycles.

trans-$Mo(N_2)_2(dppe)_2$ was prepared by one of two different methods.[6,7] Modifications were made to the latter method.[3] Hexafluorophosphoric acid–diethyl ether complex, ethyl 4-chlorobutyrate, and methyl 2-chloroproprionate were purchased from Aldrich Chemical Co. and used as received. Ethyl bromoacetate was generously provided by Professor C. A. Kingsbury of this department. Ethyl iodoacetate and ethyl 4-iodobutyrate were prepared from their corresponding chlorides by a published procedure.[8]

Infrared spectra were obtained on a Perkin-Elmer 621 grating spectrophotometer from samples prepared as indicated in the text. Proton NMR spectra were recorded in the deuterated solvents indicated on either a Varian A-60D or a Varian XL-100 NMR spectrometer. Electronic absorption data were recorded on a Cary 14 or Beckman DB-G spectrophotometer in 1.0-cm Lightpath Cells, Inc., solution cells. Melting points (mp) or decomposition points (dp) were measured in sealed, evacuated capillaries in a Meltemp apparatus and are uncorrected.

Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Inc., Woodside, N.Y.

Syntheses. Chloro[((ethoxycarbonyl)methyl)hydrazido]bis[1,2-bis(diphenylphosphino)ethane]molybdenum Tetrafluoroborate, $[MoCl(N_2HCH_2COOC_2H_5)(dppe)_2]BF_4$ (3). Ethyl chloroacetate (0.23 mL, 2.33 mmol) was added to **1** (0.736 g, 0.776 mmol) in benzene (165 mL) in a 250 mL round-bottomed flask. The solution was stirred (5 h) under a dinitrogen atmosphere under room fluorescent lighting. Ethanol (250 mL) containing 1 mL of 48% aqueous tetrafluoroboric acid was added, and the solution was stirred (0.5 h). The volume was reduced to 100 mL and a yellow solid filtered off. The red-orange filtrate was further reduced to 25 mL, and heptane (100 mL) was added to precipitate a red solid, which was filtered off and extracted with benzene (275 mL). Heptane (90 mL) was added to the combined filtrate, and a pink solid was removed by filtration. The yellow filtrate was further reduced to 50 mL and heptane (200 mL) was added. The resulting tan product was filtered off, washed with heptane, and dried in vacuo to yield **3** (0.32 g, 37%), dp 134 °C. Anal. Calcd for $[MoCl(N_2HCH_2COOC_2H_5)(dppe)_2]BF_4$, $C_{56}H_{56}BClF_4MoN_2O_2P_4$: C, 59.46; H, 4.99; N, 2.48; total halogen, 9.85. Found: C, 59.10; H, 5.06; N, 2.62; total halogen, 9.50.

The nitrogen-bound hydrogen was exchanged with deuterium by dissolving the hydrazido complex in benzene (50 mL) and adding deuterium oxide (2 mL). Following vigorous stirring of the mixture (1.5 h), the benzene layer was separated and dried ($MgSO_4$) and the product precipitated with heptane (70 mL, 0.5 h) and dried in vacuo.

Bromo[((ethoxycarbonyl)methyl)hydrazido]bis[1,2-bis(diphenylphosphino)ethane]molybdenum Tetrafluoroborate, $[MoBr(N_2HCH_2COOC_2H_5)(dppe)_2]BF_4$ (5). Ethyl bromoacetate (0.453 g, 2.712 mmol) was added to **1** (1.336 g, 1.408 mmol) dissolved in benzene (125 mL). After evacuation (−196 °C), the solution was stirred (5 h) under its own vapor pressure while irradiated by three 150-W tungsten-filament lamps (ca. 25 cm away). The volume of solution was reduced to ca. 75 mL and methanol (125 mL) added. After 1 h, the yellow solid that had formed was filtered off and 0.3 mL of 48% aqueous tetrafluoroboric acid was added to the filtrate. The color rapidly changed from orange to yellow-brown. As the solvent was removed (water aspirator), the color became red and a red solid resulted, which was dissolved in benzene (125 mL). Heptane was added in portions until a red oil formed. The brown-orange solution was decanted from the oil and evaporated to a brown oil. The oil was dissolved in ethanol (75 mL), and heptane (50 mL) was added in small portions. Brown product precipitated overnight (4 °C) and was filtered off, washed with heptane, and dried in vacuo. A second fraction was obtained from the filtrate by adding more heptane. Total yield of **5** was 0.55 g (33%); mp 133 °C. Anal. Calcd for $[MoBr(N_2HCH_2COOC_2H_5)(dppe)_2]BF_4\cdot{}^1/_2C_6H_6$, $C_{59}H_{59}BBrF_4MoN_2O_2P_4$: C, 58.34; H, 4.90; N, 2.31; total halogen, 12.84. Found: C, 58.41; H, 4.85; N, 2.11; total halogen, 12.45.

The yellow solid isolated after adding methanol was washed with ethanol and diethyl ether and identified as $MoBr_2(dppe)_2$, mp 274 °C. Anal. Calcd for $MoBr_2(dppe)_2\cdot C_6H_6$, $C_{58}H_{54}Br_2MoP_4$: C, 61.61; H, 4.81; Br, 14.13. Found: C, 61.64; H, 5.03; Br, 13.61. Crystals of the dibromide can be obtained from a dichloromethane/methanol solution.

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Iodo[((ethoxycarbonyl)methyl)hydrazido]bis[1,2-bis(diphenylphosphino)ethane]molybdenum Tetrafluoroborate, [MoI($N_2HCH_2COOC_2H_5$)(dppe)$_2$]BF_4 (7). This compound was prepared analogously to **5**, with ethyl iodoacetate (0.356 g, 1.665 mmol), **1** (1.470 g, 1.549 mmol), and benzene (150 mL), except that ethanol (250 mL) rather than methanol was added before the addition of acid. The final tan product was recrystallized from an ethanol/heptane solution to produce **7** (0.36 g, 19%), mp 135 °C. Infrared and proton NMR spectra data support this formulation.

Bromo[((ethoxycarbonyl)methyl)diazenido]bis[1,2-bis(diphenylphosphino)ethane]molybdenum, [MoBr($N_2CH_2COOC_2H_5$)(dppe)$_2$] (4). Compound **5** (0.254 g, 0.208 mmol) was dissolved in ethanol (60 mL) and 40 mL of ethanolic sodium hydroxide (ca. 0.2 g) solution was added (both solutions were filtered before mixing). The solution immediately changed from a yellow-brown to orange. Upon cooling of the solution (0 °C, 0.5 h), orange microcrystals formed and were filtered off and washed with ethanol and dried under dinitrogen. Yield of **4** was 0.14 g (64%); dp 143 °C. Anal. Calcd for MoBr($N_2CH_2COOC_2H_5$)(dppe)$_2$, $C_{56}H_{55}BrMoN_2O_2P_4$: C, 61.83; H, 5.10; N, 2.58; Br, 7.35. Found: C, 61.36; H, 5.10; N, 2.68; Br, 7.61.

Chloro[((ethoxycarbonyl)methyl)diazenido]bis[1,2-bis(diphenylphosphino)ethane]molybdenum, MoCl($N_2CH_2COOC_2H_5$)(dppe)$_2$ (2). Orange, crystalline **2** (dp 168 °C) was prepared analogously to **4**. Anal. Calcd for MoCl($N_2CH_2COOC_2H_5$)(dppe)$_2$, $C_{56}H_{55}ClMoN_2O_2P_4$: C, 64.47; H, 5.31; N, 2.68; Cl, 3.40. Found: C, 63.55; H, 5.23; N, 2.50; Cl, 3.48.

Iodo[((ethoxycarbonyl)methyl)diazenido]bis[1,2-bis(diphenylphosphino)ethane]molybdenum, MoI($N_2CH_2COOC_2H_5$)(dppe)$_2$ (6). A 10% excess of ethyl iodoacetate was added to **1** (1.857 g, 1.957 mmol) in benzene (150 mL). After evacuation (−196 °C), the solution was stirred (110 h) under its own vapor pressure. Methanol (200 mL) was added and the dark red-orange crystals that formed (1.5 h) were filtered off. The filtrate was reduced to a small volume and the resulting orange solid filtered off. The yellow filtrate was evaporated to dryness and washed thoroughly with heptane. This product, **10** (0.64 g, 28%), appeared to be the methanolate adduct of **6**: ν(CO) 1739 cm^{-1}; $\nu(CH_3OH)$ 2794 and 1098 cm^{-1}. The dark red-orange crystals (IR 1981 and 1960 cm^{-1} (KBr); 1974 cm^{-1} (CH_2Cl_2)) are believed to be cocrystallized **1** and MoI_2(dppe)$_2$.[3,9]

Compound **10** (0.428 g, 0.367 mmol) was dissolved in 2-propanol (100 mL) and filtered. Slowly (2 h) orange crystals began to form and were filtered off, washed with 2-propanol, and dried in vacuo. This product was identified as **6** (0.17 g, 41%), dp 160 °C. Anal. Calcd for MoI($N_2CH_2COOC_2H_5$)(dppe)$_2$, $C_{56}H_{55}IMoN_2O_2P_4$: C, 59.27; H, 4.89; N, 2.47; I, 11.18. Found: C, 59.78; H, 5.14; N, 2.59; Br, 10.93.

Deprotonation of **7** to yield **6** using ethanolic sodium hydroxide solution by the method given above for the preparation of **2** and **4** could also be used.

Iodo[((3-ethoxycarbonyl)propyl)hydrazido]bis[1,2-bis(diphenylphosphine)ethane]molybdenum Tetrafluoroborate, [MoI($N_2HCH_2CH_2CH_2COOC_2H_5$)(dppe)$_2$]$BF_4$ (9). A twofold excess of ethyl 4-iodobutyrate was added to **1** (1.530 g, 1.613 mmol) in benzene (250 mL). The solution was stirred (38 h) under dinitrogen under normal room fluorescent lighting. The volume of the dark orange-brown solution was reduced to 50 mL and ethanol (150 mL) containing 1.5 mL of 48% aqueous tetrafluoroboric acid was added. The resulting yellow solid was filtered off. The brown filtrate was reduced to ca. 75 mL and green-tan crystals of **9** were filtered off, washed with heptane, and dried in vacuo. The product **9** (0.77 g, 38%), dp 144 °C, was identified on the basis of infrared and proton NMR spectra (see Table I).

Iodo[((3-ethoxycarbonyl)propyl)diazenido]bis[1,2-bis(diphenylphosphino)ethane]molybdenum, MoI($N_2CH_2CH_2CH_2COOC_2H_5$)(dppe)$_2$ (8). Deprotonation of **9** (0.404 g, 0.323 mmol) was carried out with sodium hydroxide (vide supra) to yield orange **8** (0.11 g, 29%), dp 183 °C. Identification was based upon infrared and proton NMR spectra (see Table I).

Lack of Reaction between 1 and Ethyl 4-Chlorobutyrate. Ethyl 4-chlorobutyrate (0.48 g, 3.19 mmol) was added to **1** (1.60 g, 1.68 mmol) in benzene (250 mL). The solution was stirred (46 h) under dinitrogen under normal room fluorescent lighting. The infrared spectrum of an aliquot showed unreacted **1** present. A tenfold excess of ester was added and irradiation (Pyrex round-bottomed flask) was carried out with a Xenon arc lamp for 12 h. Following workup without adding acid, unreacted **1** was recovered in large yield and no evidence for a diazenido or hydrazido complex was found.

Results

The reaction of ethyl haloacetates with $Mo(N_2)_2$(dppe)$_2$, **1**, produces ((ethoxycarbonyl)methyl)diazenido complexes (eq 3; X = Cl, Br, or I) in which the halogen atom occupies a

$$\begin{aligned} Mo(N_2)_2(\mathrm{dppe})_2 + XCH_2COOC_2H_5 \rightarrow \\ MoX(N_2CH_2COOC_2H_5)(\mathrm{dppe})_2 + N_2 \quad (3) \end{aligned}$$

coordination site trans to the ((ethoxycarbonyl)methyl)diazenido ligand within the octahedral polyhedron.[3] Generally, product purification was accomplished by protonating (48% aqueous fluoboric acid) the mixture of products and isolating the ((ethoxycarbonyl)methyl)hydrazide from MoX_2(dppe)$_2$, where X = Cl, Br, or I, depending upon the particular halo ester being used in the reaction (eq 4). Infrared and ^{1}H NMR

$$MoX(N_2R)(\mathrm{dppe})_2 + HBF_4 \rightarrow [MoX(N_2HR)(\mathrm{dppe})_2]BF_4 \quad (4)$$

spectral data support the presence of the proton on the carbon-bound nitrogen both in solution and in the solid state.[3] Yields of MoX_2(dppe)$_2$ were often high and were isolated and collected for subsequent reduction to $Mo(N_2)_2$(dppe)$_2$.[10] Pure ((ethoxycarbonyl)methyl)diazenides were prepared by deprotonation of the corresponding hydrazide with alcoholic sodium hydroxide solution. Deprotonation with triethylamine in nonaqueous solution was found to be incomplete. Compound **6** was purified by isolating a methanol adduct, **10**, rather than protonating to form a hydrazide. It has been shown[1] that many alkyldiazenides of molybdenum form a methanol adduct in which strong hydrogen bonding arises between the carbon-bound nitrogen atom and the protic methanol hydrogen atom. The net effect is to produce a pseudo-hydrazide that enables purification to be accomplished without the protonation–deprotonation steps. Crystals of **6** were obtained from a 2-propanol solution of the methanol adduct **10**.

All diazenides reported here are orange, whereas the hydrazides are tan or brown. All the new compounds are air stable in the solid state but are less stable in solution than the alkyldiazenides and alkylhydrazides that do not have a functional group on the α-carbon. Infrared, ^{1}H NMR, and electronic absorption data are given in Table I.

Discussion

Simple alkyl bromides and iodides react with **1** to form alkyldiazenides in high yield.[1,3] However, simple alkyl chlorides do not react, or if they do it is to form $MoCl_2$(dppe)$_2$ rather than an alkyldiazenide.[11] More reactive alkyl halides such as benzyl and triphenylmethyl halides react rapidly to give MoX_2(dppe)$_2$ for chloride, bromide, and iodide.[9,12] These data are in agreement with the proposed mechanism for the reaction of alkyl halides with **1**.[9,12] Ethyl haloacetates fall between the two previously mentioned classes of halides. The carbon–halogen bond is more reactive toward homolytic bond cleavage than simple alkyl halides such as butyl halides but less reactive than benzyl and triphenylmethyl halides.[13] It is this increased propensity for homolytic carbon–chlorine bond cleavage compared with the case of butyl chloride, for example, that enables ethyl chloroacetate to react with **1** to form the ((ethoxycarbonyl)methyl)diazenide. The dichloride, $MoCl_2$(dppe)$_2$, is also formed during the reaction (as are the other dihalides in the reactions of the other ethyl haloacetates with **1**). In order to check that the ester group was only exerting an electron-withdrawing effect upon the carbon–chlorine bond and not interacting with the metal to promote the reaction, for example, we treated ethyl 4-chlorobutyrate with **1**. No reaction was observed. On the other hand, ethyl 4-iodobutyrate reacted predictably to give the corresponding alkyldiazenide.

Table I. Spectral Data

	IR,[b] cm^{-1}					^{1}H NMR,[c] τ					electronic absorption	
compd[a]	ν(NN) (br)	ν(NH)(br)	ν(CO)	other	phase	alkyl	CH$_2$(N)	NH[d]	CH$_2$(P)	phenyl	solvent[e]	λ_{max}, nm (ϵ_{max}, M^{-1} cm^{-1})
MoCl(N$_2$R)(dppe)$_2$, **2**	1506 vs		1737 s	1176 vs	CsI	6.16 q, 8.89 t	7.69 s		7.0–7.5 s	2.4–3.1 m	benzene	330 (6150)
MoBr(N$_2$R)(dppe)$_2$, **4**	1509 vs		1739 s	1177 vs	CsI	6.16 q, 8.88 t	7.73 s		6.9–7.5 s	2.4–3.1 m	benzene	343 (5250), 510 (166)[f]
MoI(N$_2$R)(dppe)$_2$, **6**	1505 vs		1741 s	1175 vs	CsI	6.18 q, 8.88 t	7.84 s		6.7–7.5 s	2.2–3.2 m	benzene	358 (5870), 415 (3210),[f] 488 (360)[f]
MoI(N$_2$R')(dppe)$_2$, **8**	1557 s		1732 s		KBr	5.91 q, 8.1–8.5 m, 8.6–8.9 m, 9.1–9.4 m			6.8–7.5 d	2.5–3.1 m		
[MoCl(N$_2$HR)(dppe)$_2$]BF$_4$, **3**	N.a.	3305 w (2452 w)[g]	1743 s	1215 s, 1000–1100 vs, br	CsI	6.17 q, 8.90 t	7.79 d	3.90 br, s	6.8–7.4 t	2.4–3.1 m	THF	310 (4820)[f]
[MoBr(N$_2$HR)(dppe)$_2$]BF$_4$, **5**	N.a.	3302 w	1747 s	1206 s, 1000–1100 vs, br	CsI	6.17 q, 8.89 t	7.83 d	4.02 br, s	6.5–7.3 s	2.4–3.0 m	THF	294 (9060),[f] 399 (443),[f] 550 (42)
[MoI(N$_2$HR)(dppe)$_2$]BF$_4$, **7**	N.a.	3280 w	1741 s	1204 s, 1000–1100 vs, br	KBr	6.13 q, 8.87 t	7.89 d	4.65 br, s	6.5–7.3 s	2.4–3.0 m	THF	309 (8070)[f]
[MoI(N$_2$HR')(dppe)$_2$]BF$_4$, **9**	N.a.	3265 w	1732 s	1000–1100 vs, br	KBr	5.92 q, 8.1–8.4 m, 8.75 t, 9.1–9.4 m		5.52 br, s	6.6–7.4 d	2.4–3.0 m		

[a] R = CH$_2$COOC$_2$H$_5$; R' = (CH$_2$)$_3$COOC$_2$H$_5$. [b] N.a. = Not assigned; vs = very strong, s = strong, m = medium, w = weak, sh = shoulder. [c] Relative to Si(CH$_3$)$_4$; CDCl$_3$ solvent; s = singlet, d = doublet, q = quartet, m = multiplet, br = broad. [d] Resonance disappears upon addition of D$_2$O. [e] THF = tetrahydrofuran. [f] Shoulder. [g] ν(ND).

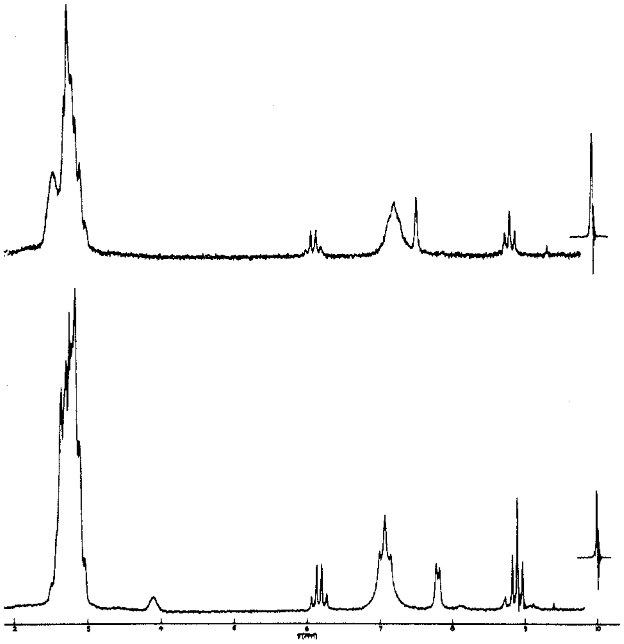

Figure 1. Proton NMR spectra of MoCl(N$_2$CH$_2$COOC$_2$H$_5$)(dppe)$_2$ (upper) and [MoCl(N$_2$HCH$_2$COOC$_2$H$_5$)(dppe)$_2$]BF$_4$ (lower) in CDCl$_3$ solution. The in situ Me$_4$Si resonance appears on the right in each spectrum.

Selected infrared spectral data of the ((ethoxycarbonyl)methyl)diazenides and hydrazides, together with a (3-(ethoxycarbonyl)propyl)diazenide and hydrazide are given in Table I. The ((ethoxycarbonyl)methyl)diazenides **2**, **4**, and **6** all exhibit a very strong absorption band at ca. 1507 cm^{-1} due to ν(NN) and a strong ν(CO) band at ca. 1739 cm^{-1}. There appears to be no effect of changing the trans halogen atom upon the ν(NN) frequency. However, the presence of the electron-withdrawing ester group attached to the α-carbon of the alkyldiazenido ligand does move the ν(NN) band to lower energy. This is most easily seen by comparison with **8** (ν(NN) 1557 cm^{-1}) in which the ester group is now on the γ-carbon of a propyldiazenido ligand. The ν(NN) stretch of this latter compound is more similar to other simple alkyldiazenido derivatives of molybdenum.[1,3] The ν(CO) stretching frequency remains essentially constant among **2**, **4**, and **6** as well as the hydrazides **3**, **5**, and **7**, whereas the parent ethyl haloacetate ν(CO) bands are quite different (ν(CO): (Cl) 1754 cm^{-1}; (Br) 1743 cm^{-1}; (I) 1730 cm^{-1}). As mentioned previously,[1,3] protonation of alkyldiazenides to form hydrazides causes a shift to lower energy of the ν(NN) band, but it has not been possible to unambiguously assign a new ν(NN) stretch in the infrared spectrum. This present work sheds no new light on the matter. In the spectra of **2**, **4**, and **6**, there is an intense band at ca. 1176 cm^{-1} which is assigned to ν(C–O).[14] A similar intense band occurs in the corresponding hydrazides **3**, **5**, and **7**, at ca. 1208 cm^{-1} which is also assigned to ν(C–O).

All four hydrazides, **3**, **5**, **7**, and **9**, as the tetrafluoroborate salts, display a broad weak to medium-weak band in the 3265–3305-cm^{-1} region. This band is assigned to ν(NH) and has also been observed in all other tetrafluoroborate and iodide salts of alkylhydrazido complexes of molybdenum.[1,3] Upon deuteration, the band is observed to shift to 2452 cm^{-1}, which arises from ν(ND). The similarity of the ν(NH) frequency to those of other alkylhydrazides without function groups and the near invariance of the ν(CO) stretch upon protonation to form the hydrazides show that the proton is associated with the carbon-bound nitrogen atom and not the carbonyl oxygen atom or bifurcated between the two atoms. The ^{1}H NMR data for compounds **2** to **9** are listed in Table I. The spectra of **2** and **3** are shown in the Figure 1. The aromatic protons display a broad multiple between ca. τ 2.2 and 3.2 for compounds **2** to **9**. The ethyl protons of all the diazenides and hydrazides appear as a well-defined triplet and a quartet (see Table I). The dppe methylene protons of the ((ethoxycarbonyl)methyl)diazenides and -hydrazides appear as a broad multiplet at between ca. τ 6.5 and 7.5 (although **3** exhibits a triplet, see Figure 1) while **6** and **7** exhibit a broad doublet for these protons which has also been observed for other simple alkyldiazenides and -hydrazides of molybdenum.[1,3] The chemical shift of nitrogen-bound methylene protons of **2** to **7** changes with variation in the coordinated halogen atom as well as shows a difference between the corresponding diazenides and hydrazides. The resonance for the ((ethoxycarbonyl)methyl)diazenido methylene protons appears as a singlet and moves to lower field as the electronegativity of the halogen increases (see Table I). There are two effects observed when **2**, **4**, and **6** are protonated. First, the methylene protons appear as a doublet due to coupling with the nitrogen-bound proton. This would suggest that the position of the protonation is the carbon-bound nitrogen atom rather than the molybdenum-bound nitrogen atom. Second, the methylene proton resonance moves to higher field. These changes are small but reproducible.

The position of the N–H resonance is a function of the coordinated halogen atom and, more dramatically, of the alkyl group attached to the same nitrogen atom. For example, the N–H resonances shows a change of ca. 0.35 ppm upon changing from the chloro to bromo to iodo derivatives. However, there is almost a 0.9 ppm change to higher field when the (ethoxycarbonyl)methyl group of **7** is replaced by a 3-(ethoxycarbonyl)propyl group (**9**). Butyl-, cyclohexyl-, and octylhydrazido complexes of molybdenum also exhibit the N–H resonance at ca. τ 6.[1,3] Considerable variation in the N–H resonance has also been observed with changes in the counterion which can be related to the hydrogen bonding ability of the counterion.[3] This effect is eliminated in these studies since the tetrafluoroborate ion is the counterion in all four hydrazides, **3**, **5**, **7** and **9**. Addition of D_2O to deuteriochloroform solutions of the hydrazides causes the N–H resonance to disappear, and for **3**, **5**, and **7**, the methylene doublet collapses to a singlet.

The electronic absorption spectra of the (ethoxycarbonyl)methyl derivatives have been recorded in benzene (diazenides) and THF (hydrazides) solutions (see Table I) and briefly mentioned elsewhere.[15] Qualitatively, the spectra are similar to those discussed previously for the simple alkyldiazenido and -hydrazido complexes of molybdenum.[1,3,15] However, the absorption maximum at ca. 345 nm of **2**, **4** and **6** does move to higher energy as the electronegativity of the halogen atom increases: Cl (330 nm), Br (343 nm), and I (358 nm). Small changes have also been observed in this same band among the simple alkyldiazenides as the trans group has been varied among I, Br, OH, N_3, and NCS.[1,3]

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Registry No. **1**, 41700-58-7; **2**, 71461-96-6; **3**, 71500-62-4; **4**, 71461-94-4; **5**, 71500-64-6; **6**, 71461-95-5; **7**, 71516-16-0; **8**, 71425-99-5; **9**, 71426-00-1; ethyl chloroacetate, 105-39-5; ethyl bromoacetate, 105-36-2; ethyl iodoacetate, 623-48-3; ethyl 4-iodobutyrate, 7425-53-8; $MoBr_2(dppe)_2$, 57088-81-0.

References and Notes

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N-Benzoyl Isocyanide Group: A π-Acceptor Ligand Similar to Carbon Monoxide and a New Route[1] to Optically Active Chromium(0) Complexes

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The photochemical synthesis of $[(arene)Cr(CO)_2CN]^-$ derivatives from $(arene)Cr(CO)_3$ complexes in the presence of KCN, followed by electrophilic attack of benzoyl chloride on the cyanide ligand, affords benzoyl isocyanide complexes of the type $(arene)Cr(CO)_2(CNCOPh)$. The spectroscopic properties (^{13}C NMR and IR) of these compounds are discussed by comparision with derivatives of the type $(arene)Cr(CO)_2L$ (L = CO, CS, $CNCH_3$, $P(OPh)_3$). These results suggest that *N*-acyl isocyanides have electronic properties close to those of carbon monoxide. Specific photochemical substitution of CO by $P(OPh)_3$ in $(arene)Cr(CO)_2(CNCOPh)$ confirms the substantial strength of the Cr^0—CNCOPh bond and provides a new route to chiral complexes. Two pairs of optically active diastereoisomers, $(C_6H_5CO_2CH_3)Cr(CO)(CNCOPh)PPh_2$(neomenthyl) and $(m\text{-}OCH_3C_6H_4CO_2CH_3)Cr(CO)(CNCOPh)P(OPh)_3$, have been prepared as synthetic applications of the latter reaction.

Introduction

Ligand substitution is probably the most important photochemical reaction of metal carbonyl derivatives. This is primarily due to the fact that photosubstitution chemistry is an essential aspect of photoinitiated transition-metal carbonyl catalysis.[2] A variety of photolabilization sites may often exist

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