Contribution from the Department of Chemistry,
University of Georgia, Athens, Georgia 30602

Organonitrogen Derivatives of Metal Carbonyls. VI. Novel Products from Reactions of 2-Bromo-2-nitrosopropane with Metal Carbonyl Anions[1,2]

R. B. KING* and W. M. DOUGLAS[3]

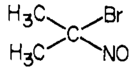
Received October 26, 1973 AIC30790K

Reaction of $NaMo(CO)_3C_5H_5$ with 2-bromo-2-nitrosopropane gives purple volatile $(CH_3)_2C(NO)Mo(CO)_2C_5H_5$. Reactions of $Na_2M_2(CO)_{10}$ (M = Cr, W) with 2-bromo-2-nitrosopropane give the yellow volatile dimethylketimine complexes $(CH_3)_2C{=}N(H)M(CO)_5$ (M = Cr, W). Reaction of $Na_2Fe(CO)_4$ with 2-bromo-2-nitrosopropane gives a mixture of yellow-orange volatile $[(CH_3)_2C{=}N]_2Fe_2(CO)_6$ and red-orange volatile $[(CH_3)_2C{=}N]_2OFe_2(CO)_6$. The structures of these new compounds are discussed.

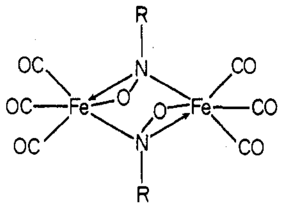
Introduction

Reactions of metal carbonyl anions with haloalkyl derivatives containing a potential donor group can yield novel transition metal organometallic derivatives containing both donor-metal and metal-carbon bonds. Thus previous papers have reported reactions of metal carbonyl anions with haloalkyl sulfides,[4] haloalkylamines,[5] and haloalkyl isocyanates.[6] The formation of *trihapto*allyl (π-allyl) derivatives[7] from metal carbonyl anions and allylic halides can also be considered as an example of a reaction of this type.

This paper describes some reactions of metal carbonyl anions with 2-bromo-2-nitrosopropane (I) which is a conveniently accessible[8] substituted nitrosoalkyl halide sufficiently stable to be isolated. We wished to see whether reactions of this type could form compounds containing metal-carbon σ bonds in which the potentially reactive nitroso group could also be made to interact with the transition metal atom. Precedent for the interaction of nitroso groups with transition metals is established in the reported compounds[9] of the type $[RNOFe(CO)_3]_2$ (II, R = aryl group) obtained by photolyses of mixtures of $Fe(CO)_5$ and nitroarenes.



I



II

The usual metal carbonyl anions[10] for forming stable derivatives containing transition metal-carbon σ bonds are $M(CO)_5^-$ (M = Mn, Re), $C_5H_5Fe(CO)_2^-$, and $C_5H_5M(CO)_3^-$ (M = Mo, W). Among these anions the molybdenum derivative $C_5H_5Mo(CO)_3^-$ was shown to react with 2-bromo-2-nitrosopropane to form a derivative $(CH_3)_2C(NO)Mo(CO)_2C_5H_5$ in which the $(CH_3)_2C(NO)$ moiety was clearly acting as a three-electron donor[11] therefore involving its nitroso group as well as a carbon atom in the bonding to the transition metal. Possibly even more interesting, however, were the unusual products formed from 2-bromo-2-nitrosopropane and the metal carbonyl dianions $M_2(CO)_{10}^{2-}$ (M = Cr, W) and $Fe(CO)_4^{2-}$, which do not normally form stable transition metal σ-alkyl derivatives by reactions with alkyl halides.. Thus the bimetallic dianions $M_2(CO)_{10}^{2-}$ (M = Cr, W) reacted with 2-bromo-2-nitrosopropane to give the complexes $(CH_3)_2C{=}NHM(CO)_5$ (M = Cr, W), the first known transition metal complexes of dimethylketimine, the imine analog of acetone which apparently is too unstable and reactive to be isolated in the pure state.[11a] Dimethylketimine thus now joins the ranks of nonisolable or unstable organic compounds such as cyclobutadiene,[12] trimethylenemethane,[13] butatriene,[14] and hydrogen isocyanide[15] which form stable metal complexes.

Experimental Section

Microanalyses and molecular weight determinations (by vapor pressure lowering) were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany, and by the microanalytical laboratory of the University of Georgia under the supervision of Mr. W. Swanson. Infrared spectra were taken in dichloromethane solutions and recorded on a Perkin-Elmer Model 621 spectrometer with grating optics. Each spectrum reported in this paper was calibrated with the 1601-cm^{-1} band of polystyrene film. Proton nmr spectra were run in $CDCl_3$ or $(CD_3)_2CO$ solutions and recorded on a Perkin Elmer Hitachi R-20 spectrometer at 60 MHz. Mass spectra were taken on the University of Georgia Perkin-Elmer Hitachi RMU-6 spectrometer at 70 eV; however, because of limitations in the available solid inlet system the only compound prepared in this paper which gave a satisfactory mass spectrum was $[(CH_3)_2C{=}NFe(CO)_3]_2$. Melting points were taken in capillaries and are uncorrected.

Tetrahydrofuran was distilled under nitrogen over sodium benzophenone ketyl immediately before use. A nitrogen atmosphere was routinely provided for the following operations: (a) carrying out reactions with organometallic compounds; (b) filling evacuated vessels containing organometallic compounds; (c)

---

[1] (a) Part V: R. B. King and A. Efraty, *J. Organometal. Chem.*, 20, 264 (1969). (b) *For a preliminary communication of some of this work see* R. B. King and W. M. Douglas, *J. Amer. Chem. Soc.*, 95, 7528 (1973).

[2] A portion of this work was presented at the 166th National Meeting of the American Chemical Society, Chicago, Ill., Aug 1973.

[3] Postdoctoral research associate, 1971-1973.

[4] R. B. King and M. B. Bisnette, *Inorg. Chem.*, 4, 486 (1965).

[5] R. B. King and M. B. Bisnette, *Inorg. Chem.*, 5, 293 (1966).

[6] R. B. King and M. B. Bisnette, *Inorg. Chem.*, 5, 306 (1966).

[7] M. L. H. Green and P. L. I. Nagy, *Advan. Organometal Chem.*, 2, 325 (1964).

[8] O. Piloty, *Ber.*, 31, 452 (1898).

[9] E. Koerner Von Gustorf and M. J. Jun, *Z. Naturforsch. B*, 20, 521 (1965); E. Koerner von Gustorf, M. C. Henry, R. E. Sacher, and C. Dipietro, *ibid.*, 1152 (1966).

[10] R. B. King, *Accounts Chem. Res.*, 3, 417 (1970).

[11] R. B. King, *Advan. Chem. Ser.*, No. 62, 203 (1967).

[11a] Note Added in Proof. After acceptance of this work for publication we were informed of the prior preparation of dialkylketimine-chromium pentacarbonyl complexes from the carbene complex $CH_3(CH_3O)CCr(CO)_5$ and oximes of dialkyl ketones as reported by E. O. Fischer and L. Knauss, *Ber.*, 103, 1262 (1970). We apologize for this earlier oversight and thank Professor Fischer for providing information on this reaction.

[12] G. F. Emerson, L. Watts, and R. Pettit, *J. Amer. Chem. Soc.*, 87, 131 (1965).

[13] G. F. Emerson, K. Ehrlich, W. P. Giering, and P. C. Lauterbur, *J. Amer. Chem. Soc.*, 88, 3172 (1966).

[14] A. Nakamura, P. J. Kim, and N. Hagihara, *J. Organometal. Chem.*, 3, 7 (1965); 6, 420 (1966).

[15] R. B. King, *Inorg. Chem.*, 6, 25 (1967).

handling filtered solutions of organometallic compounds. An H44-4GS 100-W spot lamp was used for the ultraviolet irradiations.

The 2-bromo-2-nitrosopropane was prepared[8] by bromination of acetone oxime in aqueous pyridine at 0°. After separating the blue liquid from the aqueous layer and washing several times with ice water, the blue 2-bromo-2-nitrosopropane was transferred to a round-bottom flask equipped with a vacuum-line adapter, frozen at −196°, slowly warmed up, and fractionated on a vacuum line through successive traps at −23, −45, −78, and −196°. The bulk of the 2-bromo-2-nitrosopropane passed the −23° trap and was collected in the −45° trap. *Caution!* In purifying and transferring the 2-bromo-2-nitrosopropane the temperature should be kept as low as possible. At room temperature the 2-bromo-2-nitrosopropane quickly decomposes with the evolution of much gas. At 0° decomposition occurs over a period of several hours. It is best stored in an evacuated tube at −196°.

The metal hexacarbonyls (Pressure Chemical Co., Pittsburgh, Pa.) and $Fe(CO)_5$ (GAF Corp., New York, N. Y.) were purchased from the indicated sources. A published procedure[16] was used to convert the $Fe(CO)_5$ into $Fe_3(CO)_{12}$.

Reaction of $Na[Mo(CO)_3C_5H_5]$ with 2-Bromo-2-nitrosopropane. A solution of sodium cyclopentadienide prepared by the usual procedure from 0.7 g (29 mmol) of sodium hydride and 2.0 ml (2.4 g, 36.4 mmol) of freshly distilled cyclopentadiene in 150 ml of tetrahydrofuran was boiled under reflux for 18 hr with 4.0 g (15 mmol) of $Mo(CO)_6$. The resulting yellow $Na[Mo(CO)_3C_5H_5]$ solution was cooled to −55 to −60° and then treated dropwise with a solution of 3.0 ml (3.2 g, 21 mmol) of 2-bromo-2-nitrosopropane in 150 ml of tetrahydrofuran. The reaction mixture was then allowed to warm to room temperature. Solvent was removed at ~25° (35 mm). The residue was extracted with dichloromethane (~100 ml in several portions) and then chromatographed on a 4.5 × 50 cm Florisil column. The first red band of $[C_5H_5Mo(CO)_3]_2$ was eluted with dichloromethane. After removal of $[C_5H_5Mo(CO)_3]_2$ from the chromatogram, the purple band of $(CH_3)_2C(NO)Mo(CO)_2C_5H_5$ was eluted with a 1:1 mixture of dichloromethane and diethyl ether. Solvent was removed from the eluate at ~25° (35 mm). Low-temperature recrystallization of the purple residue from a mixture of dichloromethane and hexane gave 0.50 g (11.5% yield) of purple crystalline $(CH_3)_2C(NO)Mo(CO)_2C_5H_5$. Infrared: ν(CO) in CH_2Cl_2, 1951 (s) and 1847 (s) cm^{-1}. Proton nmr in $CDCl_3$: τ 4.78 (C_5H_5, singlet), 8.33 (CH_3, singlet), and 8.39 (CH_3, singlet) of relative intensities 5:3:3, respectively. The analytical samples were purified by recrystallization from hexane and sublimation at 80° (0.01 mm).

Anal. Calcd for $C_{10}H_{11}MoNO_3$: C, 41.5; H, 3.8; Mo, 33.2; N, 4.8; O, 16.6. Found: C, 41.7; H, 3.9; Mo, 33.2; N, 4.8; O, 16.6.

Reaction of $Na_2Cr_2(CO)_{10}$ with 2-Bromo-2-nitrosopropane. A solution of $Na_2Cr_2(CO)_{10}$ was prepared by ultraviolet irradiation for 16 hr of 5.0 g (22.5 mmol) of $Cr(CO)_6$ in 400 ml of tetrahydrofuran in the presence of 20 ml of 0.75% sodium amalgam with vigorous stirring. After removal of the excess sodium amalgam the $Na_2Cr_2(CO)_{10}$ solution was treated with 3.5 ml (3.7 g, 24.3 mmol) of 2-bromo-2-nitrosopropane in 75 ml of tetrahydrofuran. After stirring for about 90 min the solvent was removed at ~25° (35 mm). A concentrated filtered solution of the residue was chromatographed on a 2 × 50 cm alumina column. The yellow band was eluted from the column with dichloromethane. The eluate was evaporated at ~25° (35 mm). Sublimation of the residue at 40–60° (0.01 mm) gave 0.24 g (4.1% yield) of yellow crystalline $(CH_3)_2C=N(H)Cr(CO)_5$, mp 45–47°. Infrared: ν(NH) in KBr, 3317 (w) cm^{-1}; ν(CO) in CH_2Cl_2, 2073 (w), 1930 (vs), and 1896 (m) cm^{-1}. Proton nmr in $(CD_3)_2CO$: τ 1.56 (NH, broad singlet) and 8.84 (CH_3, sharp singlet) of approximate relative intensities 1:6, respectively.

Anal. Calcd for $C_8H_7CrNO_5$: C, 38.5; H, 2.8; Cr, 20.8; N, 5.6; O, 32.1; mol wt 249. Found: C, 38.4; H, 2.8; Cr, 20.2; N, 5.5; O, 32.3; mol wt 249 ($CHCl_3$).

Reaction of $Na_2W_2(CO)_{10}$ with 2-Bromo-2-nitrosopropane. A solution of $Na_2W_2(CO)_{10}$ was prepared by ultraviolet irradiation for 20 hr of 6.0 g (17 mmol) of $W(CO)_6$ in 400 ml of tetrahydrofuran in the presence of 25 ml of 0.75% sodium amalgam with vigorous stirring. After removal of the excess amalgam the $Na_2W_2(CO)_{10}$ solution was treated dropwise with a solution of 4.0 ml (4.2 g, 27.7 mmol) of 2-bromo-2-nitrosopropane in 75 ml of tetrahydrofuran. After stirring for about 30 min the product $(CH_3)_2C=N(H)W(CO)_5$ was isolated from the reaction mixture by a procedure similar to the isolation of $(CH_3)_2C=N(H)Cr(CO)_5$ described above. The yield of crude product was about 0.2 g (~3%) but the careful fractional sublimation necessary to separate pure $(CH_3)_2C=N(H)W(CO)_5$ from unreacted $W(CO)_6$ reduced the yield of pure product to about 0.05 g (~0.8%). Pure $(CH_3)_2C=N(H)W(CO)_5$ is a yellow crystalline solid, mp 66–67°. Infrared: ν(NH) in KBr, 3317 (w) cm^{-1}; ν(CO) in CH_2Cl_2, 2075 (w), 1927 (vs), and ~1900 (m, sh) cm^{-1}. Proton nmr in $CDCl_3$: τ ~1.2 (extremely broad, barely observable) and 8.83 (CH_3, sharp singlet) of approximate relative intensities ~1:6, respectively.

Anal. Calcd for $C_8H_7NO_5W$: C, 25.2; H, 1.8; N, 3.7; O, 21.0; W, 48.3; mol wt 381. Found: C, 26.9; H, 2.1; N, 3.6; O, 20.3; W, 46.5; mol wt 394.

Reaction of $Na_2Fe(CO)_4$ with 2-Bromo-2-nitrosopropane. A solution of $Na_2Fe(CO)_4$ was prepared by vigorous stirring for 3.5 hr of a mixture of 6.0 g (11.9 mmol) of $Fe_3(CO)_{12}$ with 20 ml of 0.75% sodium amalgam in 400 ml of tetrahydrofuran. After removal of the excess amalgam the resulting solution was treated dropwise with a solution of 6.0 ml (6.3 g, 42 mmol) of 2-bromo-2-nitrosopropane in 75 ml of tetrahydrofuran. After stirring for 30 min, solvent was removed from the reaction mixture at ~25° (35 mm). The residue was extracted with boiling hexane. The hexane extracts were chromatographed on a 4.5 × 50 cm Florisil column. The chromatogram was developed with 500 ml of 1:1 hexane–dichloromethane. The yellow to orange band of $[(CH_3)_2C=N]_2Fe_2(CO)_6$ was then eluted with dichloromethane. After removal of this product from the chromatogram, the orange to red band of $[(CH_3)_2C=N]_2OFe_2(CO)_6$ was eluted with dichloromethane or methanol. Both eluates were evaporated to dryness at ~25° (35 mm) and the residues sublimed at ~70° (0.01 mm) to give from the first eluate ~0.20 g (~2.9% yield) of yellow $[(CH_3)_2C=N]_2Fe_2(CO)_6$, mp 111–113°, and from the second eluate ~0.15 g (~2% yield) of orange $[(CH_3)_2C=N]_2OFe_2(CO)_6$, mp 108–109°.

Properties of $[(CH_3)_2C=N]_2Fe_2(CO)_6$. (a) *Anal.* Calcd for $C_{12}H_{12}Fe_2N_2O_6$: C, 36.7; H, 3.1; Fe, 28.6; N, 7.1; O, 24.4; mol wt 392. Found: C, 36.8, 37.5; H, 3.2, 3.2; Fe, 27.2; N, 7.5, 7.0; O, 24.4; mol wt 392 ($CHCl_3$).

(b) Infrared spectrum: ν(CH) in KBr, 3000 (vvw), 2960 (vvw), 2920 (vw), and 2850 (vvw) cm^{-1}; ν(CO) in CH_2Cl_2, 2077 (m), 2029 (s), 1982 (s), and 1970 (s) cm^{-1}; ν(C=N) in KBr, 1645 (vvw) cm^{-1}; other bands in KBr, 1358 (vw), 1071 (w), 832 (w), 709 (m), 630 (m), 619 (m), 600 (m), and 578 (s) cm^{-1}.

(c) Proton nmr spectrum: singlet at τ 7.91 in $CDCl_3$ solution.

(d) Mass spectrum (relative intensities in parentheses): $[(CH_3)_2C=N]_2Fe_2(CO)_6^+$ (12), $[(CH_3)_2C=N]_2Fe_2(CO)_5^+$ (14), $[(CH_3)_2C=N]_2Fe_2(CO)_4^+$ (16), $[(CH_3)_2C=N]_2Fe_2(CO)_3^+$ (8), $[(CH_3)_2C=N]_2Fe_2(CO)_2^+$ (16), $[(CH_3)_2C=N]_2Fe_2CO^+$ (37), $[(CH_3)_2C=N]_2Fe_2^+$ (100), $(CH_3)_2C=NFe_2NH_2^+$ (31), $[(CH_3)_2C=N]_2Fe^+$ and/or $(CH_3)_2C=NFe_2^+$ (23), $(CH_3)_2C=NFeN^+$ (15), $[(CH_3)_2C=N]_2Fe_2^{2+}$ (~9), Fe_2^+ and/or $(CH_3)_2C=NFe^+$ (~27), CH_3CNFe^+ (8), $FeNH^+$ (8), and Fe^+ (10). Metastable ions at *m/e* 310.6 (w), 282.1 (w), 227 (m), 199 (s) ($[(CH_3)_2C=N]_2Fe_2(CO)_n^+ \rightarrow [(CH_3)_2C=N]_2Fe_2(CO)_{n-1}^+ + CO$; n = 5, 4, 2, 1, respectively), 150.8 (m) ($[(CH_3)_2C=N]_2Fe_2^+ \rightarrow (CH_3)_2C=NFe_2NH_2^+ + C_3H_4$), 74.7 (w) (*m/e* 168 → *m/e* 112 [several possibilities]), and 45.0 (vw) ($(CH_3)_2C=NFe^+ \rightarrow FeNH^+ + C_3H_5$).

Properties of $[(CH_3)_2C=N]_2OFe_2(CO)_6$. (a) *Anal.* Calcd for $C_{12}H_{12}Fe_2N_2O_7$: C, 35.3; H, 2.9; Fe, 27.4; N, 6.9; O, 27.4; mol wt 408. Found: C, 35.5, 34.8; H, 3.2, 2.9; Fe, 26.4; N, 7.0, 6.6; O, 28.1; mol wt 416.

(b) Infrared spectrum: ν(CH) in KBr, 3018 (vw), 2946 (vvw), 2916 (w), and 2850 (vvw) cm^{-1}; ν(CO) in CH_2Cl_2, 2075 (m), 2034 (s), and 1992 (s, br) cm^{-1}; ν(C=N) in KBr, 1648 (vvw) cm.$^{-1}$; other bands in KBr, 1364 (w), 1086 (m), 1012 (m), 950 (vw), 858 (vw), 838 (vw), 692 (m), 629 (s), 606 (m), 587 (s), and 575 (s) cm^{-1}.

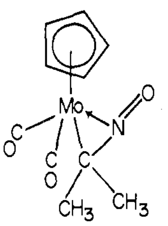
(c) Proton nmr spectrum: singlets of equal relative intensities at τ 7.41, 7.51, 8.15, and 8.35.

Discussion

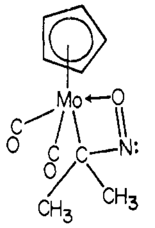
The purple product obtained from $NaMo(CO)_3C_5H_5$ and 2-bromo-2-nitrosopropane (I) of stoichiometry $(CH_3)_2C(NO)Mo(CO)_2C_5H_5$ exhibited two infrared ν(CO) frequencies in positions expected for a $C_5H_5Mo(CO)_2T$ (T = three-electron donor) derivative. Its proton nmr spectrum indicated that the two methyl groups were slightly nonequivalent. Possible structures for $(CH_3)_2C(NO)Mo(CO)_2C_5H_5$ are IIIa with the carbon and nitrogen atoms, IIIb with the carbon and oxygen atoms, IIIc with the nitrogen and oxygen atoms, and IIId with the carbon, nitrogen, and oxygen atoms, respectively, of the $(CH_3)_2C(NO)$ ligand bonded to the molybdenum atom. The available spectroscopic data on $(CH_3)_2C(NO)Mo(CO)_2C_5H_5$ do not allow

---

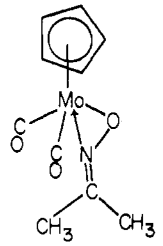
(16) W. McFarlane and G. Wilkinson, *Inorg. Syn.*, 8, 181 (1966).



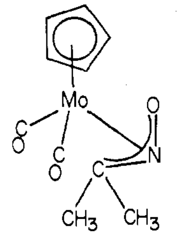
IIIa



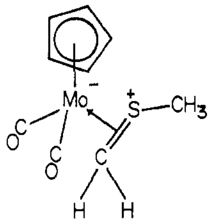
IIIb



IIIc



IIId

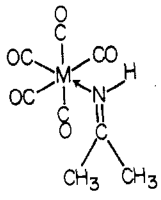


IV

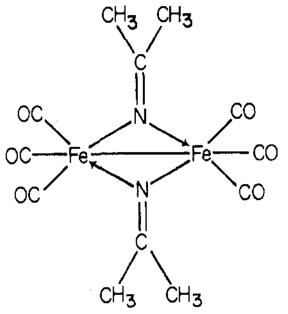
an unequivocal decision between these alternative modes of bonding the $(CH_3)_2C(NO)$ ligand to the metal atom. However, structure IIIa appears most probable in accord with the analogy of this structure to the structure IV which has been established by X-ray crystallography[17] for the related complex[4] $CH_3SCH_2Mo(CO)_2C_5H_5$.

Reactions of 2-bromo-2-nitrosopropane (I) with sodium salts of the other metal carbonyl anions which normally react with alkyl halides to give transition metal alkyls (*e.g.*, $NaW(CO)_3C_5H_5$, $NaM(CO)_5$ (M = Mn, Re), and $NaFe(CO)_2C_5H_5$)[10] failed to give any tractable products containing the $(CH_3)_2C{=}N$ or $(CH_3)_2C(NO)$ groups. The reaction of 2-bromo-2-nitrosopropane (I) with $NaW(CO)_3C_5H_5$, however, resulted in some bromination to give $C_5H_5W(CO)_3Br$. The sodium salts $Na_2M_2(CO)_{10}$ (M = Cr, W) and $Na_2Fe(CO)_4$, which normally act as reducing agents[18] rather than nucleophiles, formed novel products with 2-bromo-2-nitrosopropane (I) through deoxygenation of the nitroso group.

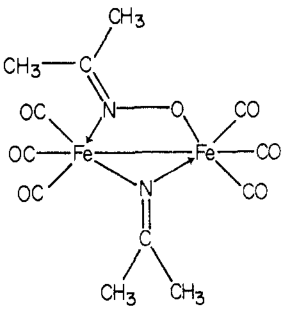
The sodium salts $Na_2M_2(CO)_{10}$ (M = Cr, W) reacted with 2-bromo-2-nitrosopropane (I) to give low yields of volatile yellow products of the stoichiometry $(CH_3)_2C{=}N(H)M(CO)_5$ (M = Cr, W). The infrared spectra of these compounds exhibited $\nu(CO)$ frequencies in the ranges 2074 ± 1, 1928 ± 2, and 1898 ± 2 cm^{-1} which may be assigned to the A_1, E, and A_1 modes of an $LM(CO)_5$ derivative[19] where the ligand L has combined donor and acceptor properties similar to an amine or alcohol. The infrared spectra of the $(CH_3)_2C{=}N(H)M(CO)_5$ derivatives also exhibited a sharp $\nu(NH)$ frequency at 3317 cm^{-1} unlike the other compounds discussed in this paper. The proton nmr spectra of the $(CH_3)_2C{=}N(H)M(CO)_5$ derivatives exhibited a broad resonance around τ 1-2 from the NH proton and a single sharp resonance around τ 8.83 ± 0.01 which can be assigned to the protons of both methyl groups which thus are equivalent. These spectroscopic data are in accord with formation of the $(CH_3)_2C{=}N(H)M(CO)_5$ derivatives as the dimethylketimine complexes V (M = Cr, W). This work represents the first time that the normally unstable dimethylketimine has been obtained as a stable metal complex.[11a]



V



VI



VII

Two products were obtained from the reaction of 2-bromo-2-nitrosopropane with $Na_2Fe(CO)_4$. The yellow less strongly absorbed product had the stoichiometry $[(CH_3)_2C{=}N]_2Fe_2(CO)_6$ as indicated not only by elemental analyses and molecular weight determination but also by its mass spectrum. The proton nmr spectrum indicated all four methyl groups in $[(CH_3)_2C{=}N]_2Fe_2(CO)_6$ to be equivalent in accord with structure VI analogous to other $[R_2NFe(CO)_3]_2$ derivatives.[20] The $(CH_3)_2C{=}N$ ligand in VI can arise from deprotonation of the dimethylketimine ligand found in the complexes V; the close relationship between these two series of complexes is thus apparent. The orange more strongly adsorbed product from 2-bromo-2-nitrosopropane (I) and $Na_2Fe(CO)_4$ had the stoichiometry $[(CH_3)_2C{=}N]_2OFe_2(CO)_6$. Its proton nmr spectrum indicated all four methyl groups to be nonequivalent in accord with a structure such as VII.

The mass spectrum of $[(CH_3)_2C{=}N]_2Fe_2(CO)_6$ (VI) was obtained. The usual stepwise loss of carbonyl groups from the molecular ion was observed. A major fragmentation pathway of the resulting carbonyl-free ion $[(CH_3)_2C{=}N]_2Fe_2^+$ was loss of a three-carbon C_3H_4 fragment. The ion $(CH_3)_2C{=}NFe^+$ underwent loss of a similar three-carbon fragment C_3H_5.

The ability of 2-bromo-2-nitrosopropane (I) to alkylate metal carbonyl anions in the normal manner[10] is suggested by its reaction with $NaMo(CO)_3C_5H_5$ to give $(CH_3)_2C(NO)Mo(CO)_2C_5H_5$ (III) which almost certainly must proceed through an unstable intermediate $(CH_3)_2C(NO)Mo(CO)_3C_5H_5$ in which the $(CH_3)_2C(NO)$ ligand is bonded to the $C_5H_5Mo(CO)_3$ group only through a molybdenum-carbon bond without involvement of the nitroso group. The limited range of tractable products obtainable from such alkylation reactions with 2-bromo-2-nitrosopropane can be attributed to the strong oxidizing properties of the nitroso group which can destroy many transition metal-organometallic systems. However, metal carbonyl anions with low nucleophilicities relative to their reducing powers such as $Na_2Fe(CO)_4$ and $Na_2M_2(CO)_{10}$ (M = Cr, W) can first deoxygenate 2-bromo-2-nitrosopropane and then undergo further reactions leading to dimethylketimine derivatives. Attempts to prepare stable transition metal-organometallic derivatives containing $(CH_3)_2C(NO)$ or $(CH_3)_2CN$ units by reactions of

---

[17] E. R. de Gil and L. F. Dahl, *J. Amer. Chem. Soc.*, 91, 3751 (1969).

[18] (a) W. J. Schlientz and J. K. Ruff, *Syn. Inorg. Metal-Org. Chem.*, 1, 215 (1971); (b) W. Hieber, J. Gruber, and F. Lux, *Z. Anorg. Allg. Chem.*, 300, 275 (1959).

[19] F. A. Cotton, *Inorg. Chem.*, 3, 702 (1964).

[20] M. Kilner, *Advan. Organometal. Chem.*, 10, 115 (1972).

2-bromo-2-nitrosopropane (I) with some of the more reactive neutral bimetallic metal carbonyl derivatives such as $Fe_2(CO)_9$, $Co_2(CO)_8$, and $[C_5H_5NiCO]_2$ were uniformly unsuccessful apparently owing to complete destruction of the transition metal–organometallic system by the strongly oxidizing nitroso group.

Acknowledgment. We are indebted to the National Cancer Institute for partial support of this work under Grants CA-12938-01 and CA-12938-02. We acknowledge the assistance of Mr. Kenneth C. Hodges with some of the infrared spectra.

Registry No. IIIa, 50986-50-0; V (M=Cr), 28394-70-9; V (M=W), 50726-12-0; VI, 50986-63-5; VII, 50986-64-6; $Mo(CO)_6$, 13939-06-5; $Cr(CO)_6$, 13007-92-6; $W(CO)_6$, 14040-11-0; $Fe_3(CO)_{12}$, 15321-51-4; 2-bromo-2-nitrosopropane, 7119-91-7.

Contribution from the Istituto Chimico
"G. Ciamician" della Universita, Bologna, Italy

Photochemistry of Mixed-Ligand Chromium(III) Complexes. III. *trans*-Chloroisothiocyanatobis(ethylenediamine)chromium(III)

M. T. GANDOLFI, M. F. MANFRIN,* A. JURIS, L. MOGGI, and V. BALZANI

Received October 9, 1973 AIC307418

The photochemical behavior of *trans*-$Cr(en)_2(NCS)Cl^+$ in aqueous solutions (pH ~3) has been investigated. Regardless of the excitation wavelength (254, 313, 365, 404, 464, 506, 549 nm), the irradiation of the complex causes the release of SCN^- and Cl^- ions and the consumption of H^+ ions. The last photoreaction is due to the detachment of one ethylenediamine end from the coordination sphere, followed by the protonation of the free amine group. Spectrophotometric and chromatographic analyses have shown that SCN^- and Cl^- are released in distinct photoreactions which lead to *cis*-$Cr(en)_2(H_2O)Cl^{2+}$ and *cis*-$Cr(en)_2(NCS)H_2O^{2+}$, respectively. The quantum yields of SCN^- ($\Phi = 0.18$) and Cl^- ($\Phi = 0.05$) release are wavelength independent, whereas the quantum yield of (one end) ethylenediamine detachment increases passing from the charge transfer ($\Phi = 0.02$) to the high-energy metal-centered bands ($\Phi = 0.05$), but it drops when the irradiation is performed in the lowest metal-centered band ($\Phi = 0.006$). The results suggest that the photoreactions leading to the release of SCN^- and Cl^- originate from the lowest quartet excited state, ^4E, whereas the photoreaction involving ethylenediamine mainly originates from the $^4B_2$ excited state. These conclusions are shown to be in agreement with the expectations based on a MO approach. The photochemical behavior of *trans*-$Cr(en)_2(NCS)Cl^+$ is compared to that of the previously investigated cis isomer.

Introduction

Recent investigations have shown that the study of the photochemical behavior of mixed-ligand Cr(III) complexes can give important information concerning the stereochemistry of the photoreaction[1] and the role played by the various excited states.[2,3] Specifically, the results of such investigations indicate that, in D_{4h}-symmetry complexes, the predominant reaction mode reflects the σ-antibonding orbital population of the lowest quartet excited state[1,2] and the photosubstitution reaction takes place with a change in the geometric configuration.[1] There is now the need to examine other mixed-ligand complexes in order to confirm the abovementioned results and elucidate more specific features of the photochemical behavior. The main problems which are still waiting a solution are the following ones: (i) the question as to what is the predominant reaction mode when the labilized axis contains two different ligands, (ii) whether the observed photoreactions originate from the same or different excited states, (iii) whether or not the CT excited states play a photochemical role, and (iv) whether π bonding is important in determining the photochemical behavior.[4,5] The reply to the above questions can only come from investigations carried out on suitably chosen systems. We wish to report here the results obtained from a systematic study on the photochemical behavior of *trans*-$Cr(en)_2(NCS)Cl^+$. A preliminary communication concerning some of the results obtained with this complex has already appeared.[6]

Experimental Section

Materials. *trans*-Chloroisothiocyanatobis(ethylenediamine)chromium(III) perchlorate, *trans*-$[Cr(en)_2(NCS)Cl]ClO_4$, was prepared following the procedure indicated in the literature.[7] The complex was recrystallized three times from cold acidic water by adding an excess of $NaClO_4$. *Anal.*[8] Calcd for $[Cr(en)_2(NCS)Cl]ClO_4$: C, 16.44; H, 4.42; Cl, 19.42; Cr, 14.24; N, 19.18; S, 8.78. Found: C, 16.33; H, 4.08; Cl, 19.47; Cr, 14.55; N, 19.05; S, 8.61. All of the other chemicals used were of reagent grade.

Apparatus. Radiations of 254, 313, 365, and 404 nm and narrow spectral bands centered at 464, 506, and 549 nm were obtained as described in ref 9. The intensity of the incident light, which was measured by means of the ferric oxalate[10] or Reineckate[11] actinometers, was of the order of 10^{-7} *Nhν*/min at each irradiation wavelength. Polychromatic radiations having wavelengths higher than 520 nm were obtained from an incandescent lamp[9] filtered with a 3-68 Corning glass filter. The photolysis cell was placed in a constant-temperature bath (±0.2°) equipped with a double quartz window to avoid moisture condensation. The absorbance measurements and the recording of the spectra were performed with an Optica CF4 NI spectrophotometer. A Knick KpH 34 pH meter was used for pH

---

[1] (a) A. D. Kirk, *J. Amer. Chem. Soc.*, 93, 283 (1971); (b) A. D. Kirk, *Mol. Photochem.*, 5, 127 (1973).

[2] S. C. Pyke and R. G. Link, *J. Amer. Chem. Soc.*, 93, 5281 (1971).

[3] S. N. Chen and G. B. Porter, *Chem. Phys. Lett.*, 6, 41 (1970).

[4] M. Wrighton, H. B. Gray, and G. S. Hammond, *Mol. Photochem.*, 5, 164 (1973).

[5] J. I. Zink, *J. Amer. Chem. Soc.*, 94, 8039 (1973).

[6] M. T. Gandolfi, M. F. Manfrin, L. Moggi, and V. Balzani, *J. Amer. Chem. Soc.*, 94, 7152 (1972).

[7] W. W. Fee, J. N. MacB. Harrowfield, and W. G. Jackson, *J. Chem. Soc. A*, 2612 (1970).

[8] Performed by A. Bernhardt, Elbach, West Germany.

[9] M. F. Manfrin, M. T. Gandolfi, L. Moggi, and V. Balzani, *Gazz. Chim. Ital.*, in press.

[10] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, 235, 518 (1956).

[11] E. E. Wegner and A. W. Adamson, *J. Amer. Chem. Soc.*, 88, 394 (1966).