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Organonitrogen Derivatives of Metal Carbonyls. VII. Some 1,3-Diphenyltriazenidometal Carbonyl and Nitrosyl Derivatives[1,2]

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Sodium 1,3-diphenyltriazenide reacts with the metal hexacarbonyls $M(CO)_6$ (M = Cr, Mo, W) in boiling 1,2-dimethoxyethane to give the corresponding orange anions $[(C_6H_5)_2N_3M(CO)_4]^-$ (M = Cr, Mo, W), isolable as their tetramethylammonium salts. Sodium 1,3-diphenyltriazenide reacts with the metal pentacarbonyl bromides $M(CO)_5Br$ (M = Mn, Re) to give the corresponding neutral derivatives $(C_6H_5)_2N_3M(CO)_4$ (M = Mn, Re). Sodium 1,3-diphenyltriazenide reacts with $C_5H_5Mo(CO)_3Cl$, $[C_5H_5Mo(CO)_3]_2$, or $CH_3Mo(CO)_3C_5H_5$ to give orange $C_5H_5Mo(CO)_2N_3(C_6H_5)_2$. Sodium 1,3-diphenyltriazenide reacts with $C_5H_5Co(CO)(C_3F_7)I$ to give orange $C_5H_5Co(C_3F_7)N_3(C_6H_5)_2$. 1,3-Diphenyltriazene reacts with $[C_5H_5Mo(NO)I_2]_2$ in dichloromethane at room temperature to give red-brown $C_5H_5Mo(NO)[N_3(C_6H_5)_2]I$.

Introduction

Recent interest in the chemistry of the uninegative bidentate nitrogen donor ligand bis(pyrazolyl)borate,[4] $H_2B(C_3H_3N_2)_2^-$, makes of interest the chemistry of other uninegative bidentate nitrogen donor ligands. One such ligand is 1,3- diphenyltriazenide, of which simple copper(I),[5] nickel(II),[6] and cobalt(III)[7] derivatives as well as ruthenium, rhodium, and iridium derivatives also containing tertiary phosphine and/or olefin ligands[8] are known. This paper reports the preparation of some new types of 1,3-diphenyltriazenidometal carbonyl, nitrosyl, and cyclopentadienyl derivatives.

Experimental Section

Microanalyses (Table I) were carried out by Atlantic Microlab, Inc., Atlanta, Ga. Molecular weight determinations (Table I) were carried out by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., using vapor pressure osmometry in benzene solution. Infrared spectra in the 2200–1500-cm^{-1} ν(CO) and ν(NO) regions (Table II) were taken in dichloromethane solutions and recorded on a Perkin-Elmer Model 621 spectrometer with grating optics. Each spectrum was calibrated against the 1601-cm^{-1} band of polystrene film. Proton nmr spectra (Table II) were taken in $CDCl_3$ or $(CD_3)_2CO$ solutions and recorded on a Varian HA-100 spectrometer operating at 100 MHz. Melting and decomposition points (Table I) were taken on samples in capillaries flushed with nitrogen and sealed with stopcock grease and are uncorrected.

A nitrogen atmosphere was routinely provided for the following operations: (a) carrying out reactions with sodium 1,3-diphenyltriazenide and/or transition metal organometallic derivatives; (b) handling filtered solutions of organometallic compounds; (c) filling evacuated vessels containing organometallic compounds. Tetrahydrofuran and 1,2-dimethoxyethane were purified by distillation over sodium benzophenone ketyl in a nitrogen atmosphere. Other solvents (*e.g.*, dichloromethane and water) were saturated with nitrogen before introduction into organometallic systems.

The 1,3-diphenyltriazene (Eastman), metal hexacarbonyls (Pressure Chemical Company, Pittsburgh, Pa.), $Fe(CO)_5$ (GAF Corp., New York, N. Y.), $Co_2(CO)_8$ (Strem Corp., Danvers, Mass.), and $CH_3C_5H_4Mn(CO)_3$ (Ethyl Corp., New York, N. Y.) were purchased from the indicated commercial sources. The compounds $Mn_2(CO)_{10}$,[9] $Mn(CO)_5Br$,[10] $Re(CO)_5Br$,[11] $C_5H_5Mo(CO)_3Cl$,[12] $[C_5H_5Mo(CO)_3]_2$,[13] $CH_3Mo(CO)_3C_5H_5$,[14] $C_5H_5Fe(CO)_2I$,[15] $C_5H_5Co(CO)(C_3F_7)I$,[16] and $[C_5H_5Mo(NO)I_2]_2$[17] were prepared by the cited published procedures.

Preparation of the Salts $[(CH_3)_4N][(C_6H_5)_2N_3M(CO)_4]$ (M = Cr, Mo, W). A mixture of 0.78 g (4.0 mmol) of 1,3-diphenyltriazene, 0.37 g (7.7 mmol) of ~50% sodium hydride dispersion in mineral oil, and 30 ml of 1,2-dimethoxyethane was stirred at room temperature until hydrogen evolution ceased (about 1 hr was sufficient). The resulting dark red solution of sodium 1,3-diphenyltriazenide was boiled under reflux with 4.0 mmol of the metal hexacarbonyl for 23 hr (M = Mo) to 41 hr (M = Cr). After cooling to room temperature, the resulting reaction mixture was filtered into a nitrogen-saturated solution of 2 g (18.3 mmol) of tetramethylammonium chloride in 100 ml of water. The orange precipitate was removed by filtration, washed with 300 ml of water, and dried at 25° (0.2 mm) for 16 hr to give 64% (M = Cr) to 74% (M = Mo) yields of the corresponding $[(CH_3)_4N][(C_6H_5)_2N_3M(CO)_4]$ derivative. The analytical samples were purified by dissolving the crude product in a minimum of dichloromethane followed by reprecipitation from the filtered dichloromethane solution by addition of excess pentane and cooling.

In a larger scale preparation the tungsten derivative $[(CH_3)_4N][(C_6H_5)_2N_3W(CO)_4]$ was prepared in 86% yield by an analogous method starting with 4.68 g (23.8 mmol) of 1,3-diphenyltriazene, 2.39 g (50 mmol) of ~50% sodium hydride dispersion in mineral oil, and 8.36 g (23.8 mmol) of hexacarbonyltungsten in 150 ml of 1,2-dimethoxyethane using a 34-hr heating period and a solution of 15 g of tetramethylammonium chloride in 300 ml of water for precipitation of the product.

Reaction of $[(CH_3)_4N][(C_6H_5)_2N_3W(CO)_4]$ with Iodine. A solution of 1.132 g (2 mmol) of $[(CH_3)_4N][(C_6H_5)_2N_3W(CO)_4]$ in 60 ml of dichloromethane was treated dropwise with a solution of 1.034 g (4 mmol as I_2) of iodine in 55 ml of dichloromethane at room temperature over a period of 40 min. During the addition of the iodine solution the color of the reaction mixture changed from red-orange to red-brown and some gas evolution was observed. After stirring for 24 hr at room temperature, the reaction mixture was filtered, the residue was washed with 40–50 ml of dichloromethane, and the combined dichloromethane solutions were evaporated to dryness to give 0.787 g (52% yield) of crude brown-black $[(CH_3)_4N][W(CO)_4I_3]$. Low-temperature crystallization from a mixture of dichloromethane and hexane gave the pure product as a yellow crystalline solid.

Reaction of $Mn(CO)_5Br$ with Sodium 1,3-Diphenyltriazenide. A solution of sodium 1,3-diphenyltriazenide prepared by deprotonation of 0.591 g (3 mmol) of 1,3-diphenyltriazene with 0.253 g (5.3 mmol) of ~50% sodium hydride in mineral oil in 30 ml of 1,2-dimethoxyethane was boiled under reflux for 3 hr with 0.825 g (3 mmol) of $Mn(CO)_5Br$. Solvent was removed from the filtered reaction mixture at ~25° (35 mm). A concentrated dichloromethane solution of the residue was chromatographed on a 2.5 × 40 cm Florisil column. The yellow band of product was eluted with 1:19 dichloromethane–hexane. Evaporation of the eluate gave 0.210 g (19% yield) of $(C_6H_5)_2N_3Mn(CO)_4$. The analytical sample was purified by low-temperature crystallization from pentane.

Reaction of $Mn_2(CO)_{10}$ with Sodium 1,3-Diphenyltriazenide. A solution of sodium 1,3-diphenyltriazenide prepared by deprotonation of 1.610 g (8.2 mmol) of 1,3-diphenyltriazene with 0.860 g (18 mmol) of ~50% sodium hydride in mineral oil in 45 ml of 1,2-dimethoxyethane was stirred with 1.560 g (5.4 mmol) of $Mn_2(CO)_{10}$ for 4.5 hr at room temperature. Chromatography of the reaction mixture on Florisil as described above gave first a yellow band of $Mn_2(CO)_{10}$ eluted with 1:19 dichloromethane–hexane followed by a band of $(C_6H_5)_2N_3Mn(CO)_4$ eluted with 1:1 dichloromethane–hexane. The crude $(C_6H_5)_2N_3Mn(CO)_4$ was purified further by rechromatography on Florisil (1:19 dichloromethane–hexane eluent) followed by low-temperature crystallization from pentane to give 0.14 g (7.1% yield) of pure $(C_6H_5)_2N_3Mn(CO)_4$.

Reaction of $Re(CO)_5Br$ with Sodium 1,3-Diphenyltriazenide. A solution of sodium 1,3-diphenyltriazenide prepared by deprotonation of 0.394 g (2 mmol) of 1,3-diphenyltriazene with 0.280 g (5.8 mmol) of ~50% sodium hydride in mineral oil in 25 ml of tetrahydrofuran was stirred with 0.812 g (2 mmol) of $Re(CO)_5Br$ at room temperature for 24 hr. Tetrahydrofuran was removed at ~25° (35 mm) and the residue dried at ~25° (0.1 mm) for 3.5 hr. A concentrated hexane

Table I. New 1,3-Diphenyltriazenidometal Carbonyl and Nitrosyl Derivatives

			Analysis, %									
			C		H		N		Other		Mol wt	
Compd	Color	Mp, °C	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$[Me_4N][Ph_2N_3Cr(CO)_4]$	Red-orange	>130 dec	55.3	55.2	5.1	5.2	12.9	12.9				
$[Me_4N][Ph_2N_3Mo(CO)_4]$	Orange	~115 dec	50.2	50.0	4.6	4.7	11.7	11.6				
$[Me_4N][Ph_2N_3W(CO)_4]$	Orange	180 dec	42.4	42.5	3.9	4.0	9.9	10.0				
$Ph_2N_3Mn(CO)_4$	Orange	116–119	52.9	53.5	2.8	3.0	11.6	11.5	17.6 (O)	16.1 (O)		
$Ph_2N_3Re(CO)_4$	Yellow	150–153	38.8	39.1	2.0	2.1	8.5	8.6	13.0 (O)	12.3 (O)	494	490
$C_5H_5Mo(CO)_2N_3Ph_2$	Orange	119–120	55.2	55.2	3.7	3.7	10.2	10.1			413	416
$C_5H_5Co(C_3F_7)N_3Ph_2$	Orange	135–137	49.1	48.2	3.1	3.5	8.6	7.8	27.2 (F)	27.5 (F)	489	491
$C_5H_5Mo(NO)(N_3Ph_2)I$	Dark red	147–148	39.7	38.8	2.9	3.0	10.9	10.5	24.7 (I)	23.8 (I)	514	521

Table II. Spectroscopic Properties of 1,3-Diphenyltriazenidometal Carbonyl and Nitrosyl Derivatives

		Proton nmr spectrum		
			τ^b	
Compd	Ir spectrum,[a] ν(CO), cm^{-1}	Solvent	C_6H_5	CH_3 or C_5H_5
$[Me_4N][Ph_2N_3Cr(CO)_4]$	2004 m, 1887 s, 1853 s, 1812 s	$(CD_3)_2CO$	~2.7 m, 2.86 m, 3.18 m	6.64 s (CH_3)
$[Me_4N][Ph_2N_3Mo(CO)_4]$	2013 m, 1890 s, 1849 s, 1810 s	$(CD_3)_2CO$	2.70 m, 2.83 m, 3.16 m	6.69 s (CH_3)
$[Me_4N][Ph_2N_3W(CO)_4]$	2000 m, 1879 s, 1843 s, 1800 s	$(CD_3)_2CO$	2.68 m, 2.80 m, 3.12 m	6.68 s (CH_3)
$Ph_2N_3Mn(CO)_4$	2113 m, 2035 s, 2007 s, 1961 s	$CDCl_3$	2.74	
$Ph_2N_3Re(CO)_4$	2119 m, 2024 s, 1996 s, 1950 s	$CDCl_3$	2.72 m	
$C_5H_5Mo(CO)_2N_3Ph_2$	1978 s, 1894 s	$CDCl_3$	~2.8 m	4.34 s (C_5H_5)
$C_5H_5Co(C_3F_7)N_3Ph_2$	None	$CDCl_3$	~2.6 m	4.92 s (C_5H_5)
$C_5H_5Mo(NO)(N_3Ph_2)I$	1680[c] (m)	$CDCl_3$	~2.7 m	3.84 s (C_5H_5)

[a] m, medium; s, strong. [b] m, multiplet; s, singlet. [c] ν(NO) frequency.

solution of the residue was chromatographed on a 2.5 × 40 cm Florisil column. The yellow band of the product was eluted with pure hexane. Evaporation of the eluate gave 0.39 g (40% yield) of $(C_6H_5)_2N_3Re(CO)_4$. The analytical sample was purified by low-temperature crystallization from pentane.

Reaction of $C_5H_5Mo(CO)_3Cl$ with Sodium 1,3-Diphenyltriazenide. A solution of sodium 1,3-diphenyltriazenide was prepared by deprotonation of 0.788 g (4 mmol) of 1,3-diphenyltriazene with a large excess (25 mmol) of sodium hydride in 45 ml of tetrahydrofuran. In order to avoid a later mineral oil impurity, the mineral oil was removed from the sodium hydride dispersion used for this experiment by washing with tetrahydrofuran. This sodium 1,3-diphenyltriazenide solution was stirred with 1.124 g (4 mmol) of $C_5H_5Mo(CO)_3Cl$ for 5 hr at room temperature. Solvent was then removed from the reaction mixture at ~25° (35 mm). The residue was extracted with seven 100-ml portions of hexane. The filtered hexane extracts were evaporated to dryness at ~25° (35 mm).

The crude product was chromatographed on a 2.5 × 40 cm Florisil column prepared in hexane which had been saturated with nitrogen before use. The product was eluted rapidly with 1:3 dichloromethane–hexane. Evaporation of the eluate to dryness at ~25° (35 mm) gave 0.27 g (16% yield) of $C_5H_5Mo(CO)_2N_3(C_6H_5)_2$. The analytical sample, mp 119–120°, was purified by recrystallization from pentane.

Use of dichloromethane rather than saturated hydrocarbon solvents in any step of the isolation of $C_5H_5Mo(CO)_2N_3(C_6H_5)_2$ other than the rapid chromatography led to some decomposiion to give impure products.

Reaction of $[C_5H_5Mo(CO)_3]_2$ with Sodium 1,3-Diphenyltriazenide. A solution of sodium 1,3-diphenyltriazenide prepared by deprotonation of 0.827 g (4.2 mmol) of 1,3-diphenyltriazene with 0.545 g (11.4 mmol) of ~50% sodium hydride in mineral oil in 60 ml of tetrahydrofuran was boiled under reflux with 0.98 g (2 mmol) of $[C_5H_5Mo(CO)_3]_2$ for 2 hr. Removal of solvent at 25° (35 mm) followed by successive hexane and dichloromethane extractions gave 0.325 g (40% yield) of crude $C_5H_5Mo(CO)_2N_3(C_6H_5)_2$ identified by its ν(CO) frequencies.

Reaction of $CH_3Mo(CO)_3C_5H_5$ with Sodium 1,3-Diphenyltriazenide. A solution of sodium 1,3-diphenyltriazenide prepared by deprotonation of 0.596 g (3 mmol) of 1,3-diphenyltriazene with 0.587 g (12.2 mmol) of ~50% sodium hydride in mineral oil in 30 ml of 1,2-dimethoxyethane was boiled under reflux with 0.825 g (3.17 mmol) of $CH_3Mo(CO)_3C_5H_5$ for 6.5 hr. Evaporation of solvent at ~25° (35 mm) followed by extraction with four 125-ml portions of pentane and evaporation of the filtered pentane extracts gave 0.145 g (11% yield) of $C_5H_5Mo(CO)_2N_3(C_6H_5)_2$ identified by its infrared ν(CO) frequencies.

Reaction of $C_5H_5Co(CO)(n\text{-}C_3F_7)I$ with Sodium 1,3-Diphenyltriazenide. A solution of sodium 1,3-diphenyltriazenide prepared by deprotonation of 0.394 g (2 mmol) of 1,3-diphenyltriazene with 0.30 g (6.2 mmol) of ~50% sodium hydride in mineral oil in 30 ml of tetrahydrofuran was stirred with 0.896 g (2 mmol) of $C_5H_5Co(CO)(n\text{-}C_3F_7)I$ at room temperature for 7.5 hr. Solvent was then removed from the reaction mixture at ~25° (35 mm) and the residue dried at ~25° (0.1 mm). The residue was extracted with 700 ml of hexane in seven portions. The filtered hexane extracts were evaporated at 25° (35 mm). A concentrated solution of the residue was chromatographed on a 2.5 × 48 cm Florisil column. Elution of the chromatogram first with hexane and then with 2:3 dichloromethane–hexane removed greenish impurities. The major orange band of product was eluted with 1:1 dichloromethane–hexane and the eluate evaporated to dryness at ~25° (35 mm) to give 0.455 g (47% yield) of orange $C_5H_5Co(n\text{-}C_3F_7)N_3(C_6H_5)_2$. The analytical sample, mp 138–140°, was purified by repetition of the chromatography followed by crystallization from hexane.

Reaction of 1,3-Diphenyltriazene with $[C_5H_5Mo(NO)I_2]_2$. A mixture of 1.63 g (8.3 mmol) of 1,3-diphenyltriazene, 2.18 g (2.45 mmol) of $[C_5H_5Mo(NO)I_2]_2$, and 100 ml of dichloromethane was stirred for 24 hr at room temperature. Solvent was removed from the filtered reaction mixture at 25° (35 mm). The residue was washed with 100 ml of hexane to remove excess 1,3-diphenyltriazene and then crystallized from a mixture of dichloromethane and hexane to give a total of 1.20 g (48% yield) of red-brown crystalline $C_5H_5Mo(NO)[N_3(C_6H_5)_2]I$, mp 148–149°, collected in two crops.

Other Reactions of Sodium 1,3-Diphenyltriazenide. The following reactions of sodium 1,3-diphenyltriazenide failed to give 1,3-diphenyltriazenidometal complexes when performed using procedures similar to those given above. (a) Reaction of sodium 1,3-diphenyltriazenide with $C_5H_5Fe(CO)_2I$ in boiling 1,2-dimethoxyethane gave $[C_5H_5Fe(CO)_2]_2$ as the only identifiable iron carbonyl derivative. (b) Reaction of sodium 1,3-diphenyltriazenide with $Co_2(CO)_8$ in boiling 1,2-dimethoxyethane did not give any stable cobalt carbonyl derivatives. (c) Reaction of sodium 1,3-diphenyltriazenide with $Fe(CO)_5$ in boiling 1,2-dimethoxyethane resulted in the recovery of 1,3-diphenyltriazene without the production of any stable iron carbonyl derivatives. (d) Sodium 1,3-diphenyltriazenide did not appear to react with $Fe_2(CO)_9$ in tetrahydrofuran at room temperature over a period of about 50 hr. This reaction mixture decomposed completely upon heating.

Discussion

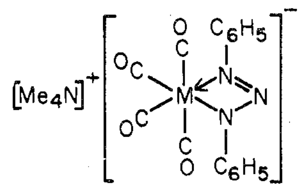
Most of the preparations of 1,3-diphenyltriazenidometal derivatives reported in this paper used reactions of the 1,-

3-diphenyltriazenide anion with appropriate transition metal derivatives. Knoth[8] in his syntheses of 1,3-diphenyltriazenido derivatives of ruthenium, rhodium, and iridium used lithium 1,3-diphenyltriazenide obtained by deprotonation of 1,3-diphenyltriazene with *n*-butyllithium. In this work we used red solutions of sodium 1,3-diphenyltriazenide in 1,2-dimethoxyethane or tetrahydrofuran, which are conveniently and rapidly obtained by stirring 1,3-diphenyltriazene with excess sodium hydride in the desired aprotic solvent for several minutes at room temperature.

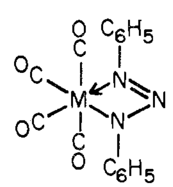
Sodium 1,3-diphenyltriazenide was found to act as the expected uninegative bidentate ligand in its thermal reactions with the metal hexacarbonyls to give the corresponding 1,3-diphenyltriazenidotetracarbonylmetalates, conveniently isolated as the tetramethylammonium salts $[(CH_3)_4N][(C_6H_5)_2N_3M(CO)_4]$ (I, M = Cr, Mo, W), which are orange relatively air-stable solids. A corresponding anionic iron carbonyl derivative could not be obtained from a corresponding reaction of sodium 1,3-diphenyltriazenide with $Fe(CO)_5$ or $Fe_2(CO)_9$ in accord with the generally greater stability of hexacoordinate relative to pentacoordinate transition metal complexes.

Some reactions of the tungsten derivative $[(CH_3)_4N][(C_6H_5)_2N_3W(CO)_4]$ with halides and other electrophilic reagents were investigated in order to see whether this tungsten derivative would function as a nucleophile like other metal carbonyl anions.[18] However, reactions of $[(CH_3)_4N][(C_6H_5)_2N_3W(CO)_4]$ with methyl iodide, allyl chloride, or trimethyltin chloride did not give tractable products. Reaction of this tungsten derivative with *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide ("Diazald") in tetrahydrofuran at room temperature gave an orange solid exhibiting ν(CO) frequencies at 2010 and 1895 cm^{-1} and a ν(NO) frequency at 1595 cm^{-1} in its infrared spectrum. This orange solid could be the carbonyl nitrosyl $(C_6H_5)_2N_3W(CO)_3NO$. However, it could not be obtained in the pure state for proper characterization.

The failure of $[(CH_3)_4N][(C_6H_5)_2N_3W(CO)_4]$ to form tractable products upon reactions with halides and other electrophiles may arise from the instability to such reagents of the 1,3-diphenyltriazenido–tungsten bond. Such an idea is supported by the observation that iodine cleaves the 1,3-diphenyltriazenido ligand from $[(CH_3)_4N][(C_6H_5)_2N_3W(CO)_4]$ at room temperature to form the known[19] $[W(CO)_4I_3]^-$ anion as the tetramethylammonium salt.



I



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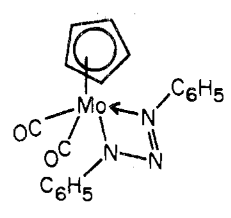


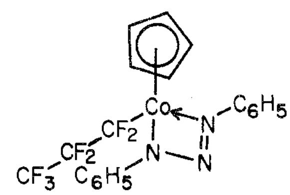
III

Neutral derivatives $(C_6H_5)_2N_3M(CO)_4$ (II, M = Mn, Re) isoelectronic with the anions $[(C_6H_5)_2N_3M(CO)_4]^-$ (M = Cr, Mo, W) are readily obtained from reactions of sodium 1,3-diphenyltriazenide with the corresponding metal pentacarbonyl bromide. The manganese derivative $(C_6H_5)_2N_3Mn(CO)_4$ is also obtained by cleavage of the manganese–manganese bond in $Mn_2(CO)_{10}$ with sodium 1,3-diphenyltriazenide. This latter reaction apparently involves elimination of $Mn(CO)_5^-$.

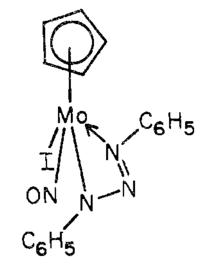
The five compounds $[(CH_3)_4N][(C_6H_5)_2N_3M(CO)_4]$ (I, M = Cr, Mo, W) and $(C_6H_5)_2N_3M(CO)_4$ (II, M = Mn, Re) are all *cis*-$L_2M(CO)_4$ derivatives. Their infrared spectra exhibit the expected four ν(CO) frequencies[20] for compounds of this type. These ν(CO) frequencies are appreciably lower in the anionic derivatives I than in the neutral derivatives II in accord with some delocalization of the negative charge (*i.e.*, extra electron density) in the anionic derivatives into the π^*-antibonding orbitals of the carbonyl groups with resulting lowering of the carbon–oxygen bond order.

The cyclopentadienylmetal carbonyl derivative $C_5H_5Mo(CO)_2N_3(C_6H_5)_2$ (III) is obtained from sodium 1,3-diphenyltriazenide and $C_5H_5Mo(CO)_3Cl$ or $[C_5H_5Mo(CO)_3]_2$. The latter reaction involves elimination of $NaMo(CO)_3C_5H_5$. Somewhat more unusual is the formation of $C_5H_5Mo(CO)_2N_3(C_6H_5)_2$ (III) rather than a methyl- or acetylmolybdenum derivative upon reaction of $CH_3Mo(CO)_3C_5H_5$ with sodium 1,3-diphenyltriazenide. The formulation of $C_5H_5Mo(CO)_2N_3(C_6H_5)_2$ (III) is supported by the expected two infrared ν(CO) frequencies and nmr resonances of the correct relative intensities for the cyclopentadienyl and phenyl rings.

All attempts to prepare a cyclopentadienyliron carbonyl derivative containing the 1,3-diphenyltriazenido ligand by reactions of $C_5H_5Fe(CO)_2I$ with sodium 1,3-diphenyltriazenide resulted instead in reduction to $[C_5H_5Fe(CO)_2]_2$, which resisted further reaction with the sodium 1,3-diphenyltriazenide. However, the cobalt derivative $C_5H_5Co(CO)(n\text{-}C_3F_7)I$ reacted readily with sodium 1,3-diphenyltriazenide to give the orange $C_5H_5Co(n\text{-}C_3F_7)N_3(C_6H_5)_2$ (IV), which is closely related to the recently reported[21] bis(pyrazolyl)borate $C_5H_5Co(n\text{-}C_3F_7)(C_3H_3N_2)_2BH_2$.



IV



V

The cyclopentadienylmolybdenum nitrosyl derivative $C_5H_5Mo(NO)[N_3(C_6H_5)_2]I$ (V) is the only compound discussed in this paper synthesized using free 1,3-diphenyltriazene rather than sodium 1,3-diphenyltriazenide as the source of the 1,3-diphenyltriazenido ligand. The formation of V from $[C_5H_5Mo(NO)I_2]_2$ and 1,3-diphenyltriazene apparently involves elimination of hydrogen iodide according to

$$[C_5H_5Mo(NO)I_2]_2 + 2(C_6H_5)_2N_3H \rightarrow 2C_5H_5Mo(NO)[N_3(C_6H_5)_2]I + 2HI$$

Attempts to replace the iodine in $C_5H_5Mo(NO)[N_3(C_6H_5)_2]I$ (V) with organic groups by reactions with phenyllithium or thallium cyclopentadienide and an attempt to prepare an iodine-free cyclopentadienylmolybdenum nitrosyl 1,3-diphenyltriazenide from $[C_5H_5Mo(NO)I_2]_2$ and sodium 1,3-diphenyltriazenide all gave negative results with generally intractable reaction mixtures.

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Registry No. $[Me_4N][Ph_2N_3Cr(CO)_4]$, 53111-38-9; $[Me_4N][Ph_2N_3Mo(CO)_4]$, 53111-40-3; $[Me_4N][Ph_2N_3W(CO)_4]$, 53111-42-5; $Ph_2N_3Mn(CO)_4$, 53111-43-6; $Ph_2N_3Re(CO)_4$, 53111-44-7;

$C_5H_5Mo(CO)_2N_3Ph_2$, 53092-57-2; $C_5H_5Co(C_3F_7)N_3Ph_2$, 53092-59-4; $C_5H_5Mo(NO)(N_3Ph_2)I$, 53092-58-3; $Cr(CO)_6$, 13007-92-6; $Mo(CO)_6$, 13939-06-5; $W(CO)_6$, 14040-11-0; $Mn(CO)_5Br$, 14516-54-2; $Mn_2(CO)_{10}$, 10170-69-1; $Re(CO)_5Br$, 14220-21-4; $C_5H_5Mo(CO)_3Cl$, 12128-23-3; $[C_5H_5Mo(CO)_3]_2$, 12091-64-4; $CH_3Mo(CO)_3C_5H_5$, 12082-25-6; $C_5H_5Co(CO)(n\text{-}C_3F_9)I$, 12128-52-8; $[C_5H_5Mo(NO)I_2]_2$, 37368-74-4; sodium 1,3-diphenyltriazenide, 53092-69-6.

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Characterization and Electrochemical Behavior of Group VI Dicarbonylbis(diphenylphosphino)methane Complexes

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The complexes *cis*-$M(CO)_2(DPM)_2$ have been characterized [M = Cr, Mo, W; DPM = bis (diphenylphosphino)methane]. Electrochemical studies show that a series of $[M(CO)_2(DPM)_2]^{0,+,2+}$ complexes exist. However, thermodynamically the equilibria for the reactions

$$\textit{cis}\text{-M(CO)}_2\text{(DPM)}_2 + \textit{trans}\text{-[M(CO)}_2\text{(DPM)}_2]^+ \overset{K_1}{\rightleftharpoons} \textit{cis}\text{-[M(CO)}_2\text{(DPM)}_2]^+ + \textit{trans}\text{-M(CO)}_2\text{(DPM)}_2$$

$$\textit{trans}\text{-[M(CO)}_2\text{(DPM)}_2]^+ + \textit{cis}\text{-[M(CO)}_2\text{(DPM)}_2]^{2+} \overset{K_2}{\rightleftharpoons} \textit{trans}\text{-[M(CO)}_2\text{(DPM)}_2]^{2+} + \textit{cis}\text{-[M(CO)}_2\text{(DPM)}_2]^+$$

lie to the left and only the cis^0, $trans^+$, and cis^{2+} species are thermodynamically stable, with the cis^+, $trans^0$, and $trans^{2+}$ species readily isomerizing. Electrochemical oxidation pathways are therefore characterized by equations of the kind

$$\textit{cis}\text{-M(CO)}_2\text{(DPM)}_2 \underset{+e}{\overset{-e}{\rightleftharpoons}} \textit{cis}\text{-[M(CO)}_2\text{(DPM)}_2]^+ \rightarrow \textit{trans}\text{-[M(CO)}_2\text{(DPM)}_2]^+$$

$$\textit{trans}\text{-[M(CO)}_2\text{(DPM)}_2]^+ \underset{-e}{\overset{+e}{\rightleftharpoons}} \textit{trans}\text{-M(CO)}_2\text{(DPM)}_2 \rightarrow \textit{cis}\text{-M(CO)}_2\text{(DPM)}_2$$

$$\textit{trans}\text{-[M(CO)}_2\text{(DPM)}_2]^+ \underset{+e}{\overset{-e}{\rightleftharpoons}} \textit{trans}\text{-[M(CO)}_2\text{(DPM)}_2]^{2+} \rightarrow \textit{cis}\text{-[M(CO)}_2\text{(DPM)}_2]^{2+}$$

Low-temperature electrochemistry reveals that at $-75°$ the rate of isomerism is slowed down considerably. Kinetically, Cr complexes are more inert than either Mo or W complexes and rate constants decrease in the order Cr < Mo < W. Oxidation state II complexes possess no inherent stability at room temperature and M(I) to M(II) electrode processes are characterized by the reaction

$$\text{[M(CO)}_2\text{(DPM)}_2]^+ \underset{+e}{\overset{-e}{\rightleftharpoons}} \text{[M(CO)}_2\text{(DPM)}_2]^{2+} \rightarrow \text{products}$$

Comparisons with the 1,2-bis(diphenylphosphino)ethane series of complexes reveal interesting thermodynamic and kinetic differences.

Introduction

A series of complexes of the general formula $[Mo(CO)_2(DPE)_2]^{0,+,2+}$ are known,[1] where M = Cr, Mo, W and DPE = 1,2-bis(diphenylphosphino)ethane. These compounds, as well as existing in different oxidation states, also exist in both cis and trans isomeric forms. The electrochemistry of these complexes has been studied.[1] Cyclic voltammetry, in particular, enables characterization of the different complexes with respect to both thermodynamic and kinetic considerations.

However, little is known about the analogous series of DPM complexes where DPM = bis(diphenylphosphino)methane. Only two complexes, namely, *trans*-$Mo(CO)_2(DPM)_2$ (*via* a reflux reaction) and *cis*-$Cr(CO)_2(DPM)_2$ (sealed tube reaction) have been reported.[2,3] The reported existence of the trans isomer rather than the cis isomer of $Mo(CO)_2(DPM)_2$ is interesting since the corresponding DPE complex, prepared *via* the same method, exists in the cis form. Conversely the predominant DPE complex of Cr isolated is the trans rather than the cis isomer. Furthermore oxidation of the complex *cis*-$Mo(CO)_2(DPE)_2$ with iodine gives a Mo(I) complex whereas the same reaction with *trans*-$Mo(CO)_2(DPM)_2$ is reported to give the *trans*-$[Mo(CO)_2(DPM)_2]^{2+}$ complex.[2] Hence considerable differences in isomeric forms, reactions, and oxidation states appear to exist, between the DPM and DPE complexes of group VI metals.

In this paper, the preparation and characterization of the