Registry No. Ni(cyclen)Cl_2, 63598-05-0; Ni(cyclen)Br_2, 63527-99-1; Ni(cyclen)$(NO_3)_2$, 63528-01-8; $[(C_2H_5)_4N]_2NiBr_4$, 1185-60-0.

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Organonitrogen Derivatives of Metal Carbonyls. 11. Studies on Cyclopentadienylmetal Dicarbonyls of Molybdenum and Tungsten Containing Ligands Derived from Diphenyltriazene and Acetone Phenylhydrazone[1]

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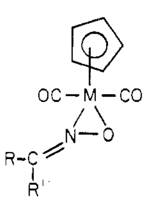
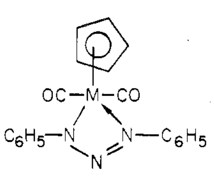
In 1974 the compound $(CH_3)_2CNOMo(CO)_2C_5H_5$ was first reported[3] as a product from the reaction of $NaMo(CO)_3C_5H_5$ with 2-bromo-2-nitrosopropane. A subsequent x-ray crystallography study[4,5] indicated structure I (M = Mo; R = R′ = CH_3) in which the nitrogen and oxygen atoms but not the carbon atom of the R_2NCO ligand are bonded to the molybdenum atom. Subsequent preparative work[1] resulted in the discovery of far more efficient and convenient methods of preparing analogues of I from a variety of ketoximes and with either molybdenum or tungsten as the central metal atom.



I



II

The success in preparing in reasonable yields a variety of ketoximato derivatives of the type I in which the oxime nitrogen and oxygen but not the ketone carbon are bonded to the metal raised the question as to whether analogous complexes could be prepared from other types of ketone derivatives. This paper describes the preparation and properties of the complexes $[(CH_3)_2CNNC_6H_5]M(CO)_2C_5H_5$ (M = Mo and W) derived from acetone phenylhydrazone. In addition, a new method for the preparation of the 1,3-diphenyltriazenido derivatives $(C_6H_5)_2N_3M(CO)_2C_5H_5$ (II, M = Mo and W) is reported. The molybdenum derivative II (M = Mo) has previously been prepared by a different method[6] but the tungsten analogue II (M = W) is reported here for the first time.

Experimental Section

Microanalyses were performed by the Atlantic Microanalytical Laboratory, Atlanta, Ga., and Galbraith Laboratories, Knoxville, Tenn. Molecular weight determinations were determined in benzene solution using a Mechrolab Model 301 vapor pressure osmometer located in the laboratory of Professor G. E. Boyd at the University of Georgia. Melting points were taken in capillaries and are uncorrected.

Infrared spectra in the ν(CO) region were taken in cyclohexane solutions and recorded on a Perkin-Elmer Model 621 spectrometer with grating optics. Each spectrum was calibrated against the 1601-cm^{-1} band of polystyrene film. Proton NMR spectra (Table I) were recorded on a Varian T-60 spectrometer at 60 MHz. Carbon-13 NMR spectra (Table I) were recorded on a Jeolco PFT-100 spectrometer operating at 25.0349 MHz with proton noise decoupling and a deuterium lock using a 5 to 8 s repetition rate. Both the proton and carbon-13 NMR spectra were run in $CDCl_3$ solutions using tetramethylsilane as an internal standard. In the carbon-13 NMR spectra chromium(III) acetylacetonate was added in ~0.15% concentration as a shiftless relaxation reagent[7] to facilitate observation of the metal carbonyl resonances.

Dichloromethane and diethyl ether were freshly distilled over phosphorus pentoxide and calcium hydride, respectively. Pyridine was dried over solid potassium hydroxide and then freshly distilled over barium oxide. Solvents were saturated with nitrogen before use in organometallic experiments. In addition, all organometallic reactions were run in a dry nitrogen atmosphere.

Reagents. 1,3-Diphenyltriazene (Eastman) and the metal hexacarbonyls (Pressure Chemical Company, Pittsburgh, Pa.) were purchased from the indicated commercial sources. Acetone phenylhydrazone, bp 99–103 °C (0.5 mm) (lit.[8] bp 108–109 °C (1.6 mm)) was prepared by reaction of phenylhydrazine with excess acetone according to a published procedure.[8] The cyclopentadienylmetal tricarbonyl chlorides, $C_5H_5M(CO)_3Cl$ (M = Mo and W), were prepared on a 0.1 mol scale by an adaptation described elsewhere[1] of the standard published method.[9]

Preparation of $[(CH_3)_2CNNC_6H_5]Mo(CO)_2C_5H_5$ (III, M = Mo). A solution of 2.3 g (15 mmol) of acetone phenylhydrazone in 300 mL of diethyl ether was treated with 7 mL of a 2.5 M hexane solution of *n*-butyllithium (17.5 mmol). The resulting deep orange solution was treated with 2.89 g (10.3 mmol) of $C_5H_5Mo(CO)_3Cl$ at -78 °C. The resulting mixture was stirred at room temperature for 4 h. The reaction mixture was then filtered through Celite. Solvent was removed from the filtrate at 25 °C (25 mm). Crystallization of the residue from a mixture of dichloromethane and hexane gave 3.1 g (85% yield) of deep red-orange $[(CH_3)_2CNNC_6H_5]Mo(CO)_2C_5H_5$. The analytical sample, mp 133–135 °C dec, ν(CO) 1953 and 1868 cm^{-1}, was purified by a second crystallization from a mixture of dichloromethane and hexane. Anal. Calcd for $C_{16}H_{16}MoN_2O_2$: C, 52.7; H, 4.4; N, 7.7. Found: C, 52.6; H, 4.5; N, 7.6.

An attempt to prepare $[(CH_3)_2CNNC_6H_5]Mo(CO)_2C_5H_5$ by reaction of 10 mmol each of acetone phenylhydrazone and $C_5H_5Mo(CO)_3Cl$ in 200 mL of pyridine at 70 °C for 5 h was unsuccessful owing to the preferential formation of a purple complex, mp 97–98 °C, identified as the pyridine derivative $C_5H_5Mo(CO)_2(NC_5H_5)Cl$ from its infrared spectrum in the 4000–5000 cm^{-1} region and its proton NMR spectrum.

Preparation of $[(CH_3)_2CNNC_6H_5]W(CO)_2C_5H_5$ (III, M = W). A solution of 1.48 g (10 mmol) of acetone phenylhydrazone in 100 mL of diethyl ether was treated with 4 mL of a 2.5 M hexane solution of *n*-butyllithium (10 mmol). After stirring for 20 min at room temperature the resulting light orange solution was treated with 2.3 g (6 mmol) of $C_5H_5W(CO)_3Cl$ and then irradiated at room temperature with a 125 W mercury ultraviolet lamp in a Pyrex well for 1 h. The resulting reaction mixture was filtered through Celite and the Celite was washed with 150 mL of diethyl ether. Evaporation of the filtrate at 25 °C (25 mm) followed by two crystallizations from mixtures of dichloromethane and hexane gave 1.3 g (48% yield) of red-orange $[(CH_3)_2CNNC_6H_5]W(CO)_2C_5H_5$, mp 154–155 °C dec, infrared ν(CO) 1944 and 1856 cm^{-1}. Anal. Calcd for $C_{16}H_{16}N_2O_2W$: C, 42.5; H, 3.5; N, 6.2; mol wt, 452. Found: C, 42.4; H, 3.5; N, 6.1; mol wt, 400.

Preparation of $(C_6H_5)_2N_3Mo(CO)_2C_5H_5$ (II, M = Mo) by the Pyridine Method. A mixture of 1.0 g (5.1 mmol) of 1,3-diphenyl-

Table I. NMR Spectra of Compounds Described in this Paper

Compd[a]	^{1}H NMR spectrum,[b] τ			^{13}C NMR spectra,[c] δ				
	C_6H_5	C_5H_5	CH_3	CO	C_6H_5	R_2CNN	C_5H_5	CH_3
$Ph_2N_3Mo(CO)_2Cp$	2.75	4.27 s		253.6	149.2, 128.6 124.1, 115.5		95.3	
$Ph_2N_3W(CO)_2Cp$	2.76	4.17 s		245.0	148.8, 128.7 124.5, 115.7		93.9	
$(Me_2CNNPh)Mo(CO)_2Cp$	2.88 t (8), 3.17 d (8), 3.46 d (8)	4.35 s	7.68 s 7.95 s	232.6, 224.2	161.6, 128.5 120.4, 117.0	159.5	95.5	23.3
$(Me_2CNNPh)W(CO)_2Cp$	2.88 t (8), 3.16 d (8), 3.48 d (8)	4.20 s	7.65 s 7.87 s	238.2, 232.3	160.4, 128.5 120.6, 116.9	160.0	94.7	23.0
$Me_2CNOMo(CO)_2Cp$[d]		4.42 s	7.90 s 7.97 s	229.0, 223.0		148.6	96.8	20.7 19.4

[a] Ph = phenyl, Me = methyl, Cp = cyclopentadienyl. [b] s = singlet, d = doublet, t = triplet; splittings in Hz are given in parentheses. [c] Since the ^{13}C NMR spectra were all proton decoupled, all observed ^{13}C resonances were singlets. [d] Data from ref 1.

triazene, 1.0 g (3.6 mmol) of $C_5H_5Mo(CO)_3Cl$, and 85 mL of pyridine was heated at 70 °C for 10 h. Pyridine was then removed from the reaction mixture at 20 °C (0.08 mm). The residue was chromatographed on a 2 × 50 cm Florisil column prepared in hexane. The major orange band was eluted with dichloromethane. Evaporation of the eluate at 20 °C (25 mm) followed by crystallization from a mixture of dichloromethane and hexane gave a total of 0.71 g (53% yield) of orange crystalline $(C_6H_5)_2N_3Mo(CO)_2C_5H_5$, mp 115 °C (lit.[6] mp 119–120 °C), infrared ν(CO) 1985 and 1911 cm.$^{-1}$

Preparation of $(C_6H_5)_2N_3W(CO)_2C_5H_5$ (II, M = W). A mixture of 2.0 g (10.1 mmol) of 1,3-diphenyltriazene, 1.8 g (4.9 mmol) of $C_5H_5W(CO)_3Cl$, and 200 mL of pyridine was irradiated for 15 h at ambient temperature in a Pyrex flask with an external ultraviolet sunlamp. Pyridine was removed from the resulting orange mixture at 25 °C (0.05 mm). The residue was chromatographed on a 2 × 50 cm Florisil column in dichloromethane solution. The major orange band was eluted with dichloromethane. Evaporation of the eluate at 25 °C (25 mm) followed by crystallization from a mixture of dichloromethane and hexane gave 1.6 g (64% yield) of red-orange $(C_6H_5)_2N_3W(CO)_2C_5H_5$. The analytical sample, mp 107–109 °C dec, infrared ν(CO) 1968 and 1887 cm^{-1}, was purified by a second crystallization from a mixture of dichloromethane and hexane. Anal. Calcd for $C_{19}H_{15}N_3O_2W$: C, 45.6; H, 3.0; N, 8.4. Found: C, 45.5; H, 3.0; N, 8.3.

Results and Dicussion

The preparations of the complexes $[(CH_3)_2CNNC_6H_5]M(CO)_2C_5H_5$ (M = Mo and W) from acetone phenylhydrazone used the following sequence of reactions:

$$(CH_3)_2C{=}NNHC_6H_5 + C_4H_9Li \rightarrow (CH_3)_2C{=}NN(Li)C_6H_5 + C_4H_{10}$$

$$(CH_3)_2C{=}NN(Li)C_6H_5 + C_5H_5M(CO)_3Cl \rightarrow [(CH_3)_2CNNC_6H_5]M(CO)_2C_5H_5 + CO + LiCl$$

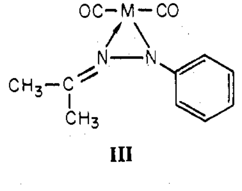
This preparative approach parallels previously reported syntheses of the ketoximato derivatives[1] I and the 1,3-diphenyltriazenido derivative[6] $(C_6H_5)_2N_3Mo(CO)_2C_5H_5$ (II, M = Mo). In accord with the previous[1] work on the ketoximato derivatives ultraviolet irradiation was necessary to effect the required decarbonylation of the tungsten derivative but not of the molybdenum derivative.

The complexes $[(CH_3)_2CNNC_6H_5]M(CO)_2C_5H_5$ (M = Mo and W) form dark red-orange solids which can be handled for short periods in air but which oxidize in air on prolonged exposure or oxidize much more rapidly in solution. Chromatography is best avoided in their preparations owing to extensive decomposition on the chromatography column. Also the molybdenum derivative was too unstable in solution to obtain a reliable molecular weight determination in the available osmometer.

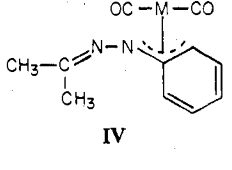
The carbon-13 NMR spectra of the complexes $[(CH_3)_2CNNC_6H_5]M(CO)_2C_5H_5$ (M = Mo and W) (Table I) suggest that the imino C=N carbon does not participate directly in the bonding to the transition metal. This carbon atom has a relatively low field chemical shift in the derivatives $[(CH_3)_2CNNC_6H_5]M(CO)_2C_5H_5$ (M = Mo and W) ($\delta \sim 160$) similar to that of the imino C=N carbon (δ 148.6) in the ketoximato complex $(CH_3)_2CNOMo(CO)_2C_5H_5$ shown by x-ray crystallography[4,5] to have the structure I (M = Mo; R = R′ = CH_3). Another feature of the carbon-13 NMR spectra of the complexes $[(CH_3)_2CNNC_6H_5]M(CO)_2C_5H_5$ (M = Mo and W) is the presence of two carbonyl resonances in accord with the asymmetry of the $(CH_3)_2CNNC_6H_5$ ligand required by any conceivable type of dihapto or trihapto bonding to the metal atom.

Both the proton and carbon-13 NMR spectra (Table I) of $[(CH_3)_2CNNC_6H_5]M(CO)_2C_5H_5$ (M = Mo and W) suggest an unusual perturbation of the phenyl rings possibly by interaction with the metal atom. The chemical shift range of the phenyl proton resonances in these complexes is unusually large providing a rare instance where the individual ortho, meta, and para proton resonances can be identified from their relative intensities and first-order splittings. Thus in the complexes $[(CH_3)_2CNNC_6H_5]M(CO)_2C_5H_5$ (M = Mo and W), the proton resonances at τ 2.88, 3.16 ± 0.01, and 3.47 ± 0.01 can be assigned to the meta, para, and ortho protons, respectively. Furthermore, in the carbon-13 NMR spectra of the complexes $[(CH_3)_2CNNC_6H_5]M(CO)_2C_5H_5$ (M = Mo and W) the phenyl resonance at δ 117.0 ± 0.1, which is assigned to the ortho carbon atom on the basis of its position, relative intensity, and comparison with the carbon-13 NMR spectrum of aniline,[10] broadens drastically upon cooling from +35 to −28 °C. This broadening is more severe in the molybdenum derivative than the tungsten derivative at a given temperature. This broadening of the ortho carbon resonance suggests that rotation of the phenyl ring around the carbon–nitrogen bond is restricted at low temperatures.

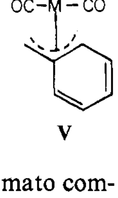
All of these spectroscopic data on the $[(CH_3)_2CNNC_6H_5]M(CO)_2C_5H_5$ (M = Mo and W) derivatives do not exclude their formulations as the *N,N*-dihapto derivatives III (M = Mo and W) completely analogous to the established *N,O*-dihapto structures for the ketoximato complexes I discussed above. However, we believe that the alternative *trihapto*-7-azabenzyl structures IV (M = Mo and W) must also be considered for these complexes in view of the unusual perturbations of the phenyl rings indicated in their NMR spectra. Such perturbations could arise from partial bonding of the phenyl rings to the metal atom. The *trihapto* benzyl derivative[11] $C_6H_5CH_2Mo(CO)_2C_5H_5$ (V) closely related to IV exhibits fluxional[12] properties above room temperature



III



IV



V

which create an effective plane of symmetry on the NMR time scale thereby making both sides of the benzene ring equivalent. By analogy the *trihapto*-7-azabenzyl derivatives IV are expected to exhibit similar fluxional properties. If the coalescence temperatures of the *trihapto*-7-azabenzyl derivatives IV are lower than that of the *trihapto*-benzyl derivative V, such fluxional properties could persist even below room temperature thereby making both sides of the benzene ring equivalent even at the lowest temperatures at which NMR spectra were taken. The broadening of the ortho carbon resonances in $[(CH_3)_2CNNC_6H_5]M(CO)_2C_5H_5$ (M = Mo and W) observed at −28 °C could arise from incipient freezing out of the fixed structure IV. The ortho carbon resonance in a fluxional compound of structure IV should broaden before the meta carbon resonance on cooling since in a frozen structure IV the bonding of the metal to an ortho carbon but to neither meta carbon would make the chemical shifts of the two ortho carbons more different than those of the two meta carbons. In our opinion the ambiguity between the *N,N-dihapto* structures III and the *trihapto*-7-azabenzyl structures IV for the complexes $[(CH_3)_2CNNC_6H_5]M(CO)_2C_5H_5$ (M = Mo and W) will only be satisfactorily resolved when x-ray structural data become available.

One of the several methods that we have used to prepare the ketoximato complexes[1] $RR'CNOM(CO)_2C_5H_5$ (I, M = Mo and W) uses the reaction of $C_5H_5M(CO)_3Cl$ (M = Mo and W) with excess ketoxime in pyridine solution at ~70 °C. An analogous reaction of $C_5H_5Mo(CO)_3Cl$ with excess acetone phenylhydrazone failed to give any $[(CH_3)_2CNNC_6H_5]Mo(CO)_2C_5H_5$ but instead gave the pyridine complex[13] $C_5H_5Mo(CO)_2(NC_5H_5)Cl$. This suggests that the $(CH_3)_2CNNC_6H_5$ ligand forms weaker chemical bonds with transition metals than the RR′CNO ligands in I.

The "pyridine method", although it fails for the preparation of $[(CH_3)_2CNNC_6H_5]Mo(CO)_2C_5H_5$ from acetone phenylhydrazone, provides an alternative to the previously reported[6] preparation of the 1,3-diphenyltriazenido complex $(C_6H_5)_2N_3Mo(CO)_2C_5H_5$ (II, M = Mo). Similarly, the ultraviolet irradiation of $C_5H_5W(CO)_3Cl$ with excess 1,3-diphenyltriazene in pyridine solution gives the previously unreported $(C_6H_5)_2N_3W(CO)_2C_5H_5$ (II, M = W). The carbon-13 NMR spectra of the 1,3-diphenyltriazenido complexes $(C_6H_5)_2N_3M(CO)_2C_5H_5$ (II, M = Mo and W) (Table I) indicate equivalence of the two metal carbonyl groups in accord with the symmetry of the 1,3-diphenyltriazenido ligand, at least on an NMR time scale.

Acknowledgment. We are indebted to the National Science Foundation for partial support of this work under Grant CHE-75-19974.

Registry No. II (M = Mo), 53092-57-2; II (M = W), 63641-12-3; III (M = Mo), 63641-13-4; III (M = W), 63641-14-5; IV (M = Mo), 63641-15-6; IV (M = W), 63641-16-7; $C_5H_5Mo(CO)_3Cl$, 12128-23-3; $C_5H_5W(CO)_3Cl$, 12128-24-4; ^{13}C, 14762-74-4.

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Thin-Layer Spectroelectrochemical Study of Tetrakis(4-*N*-methylpyridyl)porphinecobalt(III)

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Reports have recently appeared dealing with the reactions of the water-soluble metalloporphyrin tetrakis(4-*N*-methylpyridyl)porphinecobalt(III) ($Co^{III}TMpyP$) with a variety of reducing agents.[3-5] These studies led to a determination of the absorbance maximum in the Soret region for the diaquo form of $Co^{II}TMpyP$ as 429 nm and an estimate of $+0.3 \le E^{\circ\prime} \le +0.8$ V vs. NHE for $CoP(H_2O)_2^{5+} + e^- \rightarrow CoP(H_2O)_2^{4+}$. In order to determine more precisely these important parameters, we have applied the optically transparent thin-layer electrode (OTTLE) technique to this cobalt porphyrin system.[6]

Experimental Section

$(CoTMpyP)I_5$ was prepared, purified, and converted to the chloride form by methods described elsewhere.[7,8] Solutions of the porphyrin were prepared by dissolving the solid in 0.5 M $NaNO_3$/0.01 M HNO_3 in doubly distilled water. The metalloporphyrin concentration was 2.04×10^{-4} M, somewhat beyond the concentration range previously investigated for adherence to Beer's law behavior.[7] The spectral properties of these solutions lead us to conclude that monomeric $CoP(H_2O)_2$ is the only chromophore present in appreciable amounts.

Cyclic voltammetry and spectropotentiostatic experiments were performed with a potentiostat of conventional operational amplifier design, an X-Y recorder (Houston Omnigraphic Model 2000), and a digital voltmeter (Fluke Model 8000A). A Cary 14 spectrophotometer, with cell compartment modified to permit introduction of electrical leads, was used for the spectropotentiostatic experiment. The spectroelectrochemical cell was an OTTLE of the minigrid-microscope slide design.[6,9,10] The cell was constructed by sandwiching a gold minigrid electrode (500 wires/in., 60% transmittance; Buckbee-Mears Co., St. Paul, Minn.) between two glass microscope slides which were separated by Teflon tape spacers along the edges. Calibration of this OTTLE by controlled potential coulometry of a standard potassium ferricyanide solution[9] gave an electrochemical cell volume of 43 μL and an optical path of 0.022 cm. The reference and auxiliary electrodes were a saturated sodium chloride calomel electrode (H cell) and a platinum wire, respectively. The potential of the reference electrode was found to be within 2 mV of the potential of the conventional SCE (saturated with KCl).

In a typical experiment the OTTLE was first positioned in the Cary 14 cell compartment which was then purged with argon and the top sealed with clear polyethylene. The sample was deoxygenated by argon bubbling and transferred to the electrochemical cell by a previously reported method.[9] Electrochemical and spectroelectrochemical measurements were then performed while continuously flushing the cell compartment with argon.

Results and Discussion

Thin-layer cyclic voltammograms of $(Co^{III}TMpyP)^{5+}$ and of the supporting electrolyte are shown in Figure 1. A deoxygenated solution of 0.5 M $NaNO_3$/0.01 M HNO_3 gives a wide potential window extending from +0.900 to −0.450 V vs. SCE on the gold minigrid OTTLE as shown by the dotted line. The voltammogram of $(Co^{III}TMpyP)^{5+}$ exhibited well-defined reduction and oxidation waves for the $Co^{III} \rightleftarrows Co^{II}$ couple. A scan, initiated at +0.500 V vs. SCE in the negative direction, caused reduction of Co(III) to Co(II) with a cathodic peak potential (E_{pc}) of +0.135 V. Scan reversal at 0 V vs. SCE resulted in oxidation of Co(II) to Co(III) with an anodic peak potential (E_{pa}) of +0.210 V vs. SCE. Three consecutive cycles on the same solution gave identical voltammograms, indicating that the cobalt oxidation state can be reversibly cycled between III and II in the thin-layer cell. An