TABLE IV
RELATIONSHIP OF MNC ANGLES (DEG) TO K···S AND K···N DISTANCES (A) IN TWO THIOCYANATES

Compound	Angle MNC	K···S distance		K···N distance	
		Average	Shortest	Average	Shortest
$K_2Co(NCS)_4 \cdot H_2O$	111	3.66	3.59	3.24	2.62
$K_3Mo(NCS)_6 \cdot H_2O \cdot CH_3COOH$	163	3.39	3.30	>4	3.74
	169	3.39	3.33	>4	4.19
	176 (two)	3.46	3.29	>4	3.60
	166 (two)	3.45	3.25	>4	4.06

the van der Waals limit of the neighboring sulfur atom (Figure 6). The water molecule is rather close to the S(1) and S(2) atoms, the two contacts being 3.40 and 3.49 A. Consequently, a torque is applied to the ends of two ligands, NCS(1) and NCS(2). This torque would force the octahedron to rotate (counterclockwise in the figure) were it not for the other potassium ion K(1), which prevents any movement of the sulfur atom ends of the remaining four ligands, NCS(3) (two) and NCS(4) (two).

From this argument it should follow, and indeed does, that the four K(1)···S distances in the direction of the forced rotation are significantly shorter than the four distances in the reverse direction. The two MoNC(4) angles are more bent (166°) than the two MoNC(3) angles (176°), agreeing with the fact that the ends of the NCS(4) groups approach K(1) ions and neighboring NCS(1) groups more closely than the NCS(3) groups approach K(1) ions and NCS(2) groups. The bending occurs in the expected direction (see Figure 6).

Thus, the effect of the crowding of the water molecules against the S(1) and S(2) atoms is not to initiate rigid-body rotation but to cause four of the six Mo–NCS linkages to bend at the nitrogen atom. The remaining two linkages, being relatively free from steric effects, have MoNC angles which are nearest the 180° value expected for form A resonance.

Acknowledgments.—We wish to thank Dr. Robert Thomas for helpful discussions during the early part of this research. Calculations were done at the Computation Centers of Boston University and the Massachusetts Institute of Technology.

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Organometallic Chemistry of the Transition Metals. XXII. The Synthesis of Unusual Cyclopentadienylmolybdenum Nitrosyl Derivatives Using Thallium Cyclopentadienide[1,2]

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Thallium cyclopentadienide reacts with $[C_5H_5Mo(NO)I_2]_2$ in tetrahydrofuran solution to give green-black $(C_5H_5)_2Mo(NO)I$ apparently containing a novel type of allylic π-cyclopentadienyl ring. Reaction of this iodide derivative with methylmagnesium bromide gives the brown volatile σ-methyl derivative $(C_5H_5)_2Mo(NO)CH_3$. Reaction of the molybdenum nitrosyl chloride $[Mo(NO)_2Cl_2]_n$ with thallium cyclopentadienide in tetrahydrofuran solution gives yellow-green unstable $C_5H_5Mo(NO)_2Cl$. The reactivity of metal halide derivatives toward thallium cyclopentadienide is discussed.

Introduction

A common method for the synthesis of π-cyclopentadienyl derivatives is the reaction of sodium cyclopentadienide with various transition metal halides.[4] However, in some cases sodium cyclopentadienide does not give π-cyclopentadienyl derivatives with metal halides owing to destruction of the metal complex arising from the strongly reducing and basic properties of sodium cyclopentadienide. More recently thallium cyclopentadienide has been shown to be a suitable reagent for the preparation of many π-cyclopentadienyl derivatives.[5] Since thallium cyclopentadienide is a weaker reducing agent and base than sodium cyclopentadienide, certain reactions of halide derivatives which failed to give isolable π-cyclopentadienyl derivatives with sodium cyclopentadienide were reinvestigated using thallium cyclopentadienide.

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[1] For Part XXI of this series see R. B. King and M. B. Bisnette, *J. Organometal. Chem.* (Amsterdam), **8**, 287 (1967).

[2] Portions of this work were presented at the Third International Symposium on Organometallic Chemistry, Munich, Germany, Aug 1967.

[3] Fellow of the Alfred P. Sloan Foundation, 1967–1969.

[4] For a review on the synthesis of cyclopentadienylmetal derivatives see J. Birmingham, *Advan. Organometal. Chem.*, **2**, 365 (1964).

[5] A. N. Nesmeyanov, R. B. Materikova, and N. S. Kochetkova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1334 (1963); *Chem. Abstr.*, **59**, 12841*d* (1963); A. N. Nesmeyanov, K. N. Anisimov, and N. E. Kolobova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2220 (1964); *Chem. Abstr.*, **62**, 7788*b* (1965); C. C. Hunt and J. R. Doyle, *Inorg. Nucl. Chem. Letters*, **2**, 283 (1966); T. J. Katz and J. J. Mrowca, *J. Am. Chem. Soc.*, **89**, 1105 (1967).

TABLE I

NEW COMPOUNDS PREPARED IN THIS WORK

Compound	Color	Mp, °C		Analyses, %						Mol wt	Proton nmr, τ	
				C	H	N	O	Mo	X		π-C_5H_5	Other
$(C_5H_5)_2Mo(NO)I$	Green-black	157–159 dec	Calcd	31.3	2.6	3.7	4.2	25.1	33.2 (I)	383	3.82	. . .
			Found	31.1	2.9	3.8	4.3	25.0	33.2 (I)	365		
$(C_5H_5)_2Mo(NO)CH_3$	Brown	*a*	Calcd	48.7	4.8	5.2	5.9	35.4		277	4.24	8.94 (CH_3)
			Found	48.7	4.8	5.2	6.2	35.1		232		
$C_5H_5Mo(NO)_2Cl$	Yellow-green	118	Calcd	23.4	1.9	10.9	12.5	37.5	13.8 (Cl)	256.5	3.84	. . .
			Found	22.8	1.8	10.0	12.9	38.6	13.8 (Cl)	277		

[a] This compound decomposed gradually upon heating without a clearly defined melting or decomposition point.

Two complex molybdenum nitrosyl halides which fail to form π-cyclopentadienyl derivatives with sodium cyclopentadienide are the recently reported[6] $[C_5H_5Mo(NO)I_2]_2$ and the polymeric $[Mo(NO)_2Cl_2]_n$.[7] This paper describes the reactions of these materials with thallium cyclopentadienide which give the novel π-cyclopentadienyl derivatives $(C_5H_5)_2Mo(NO)I$ and $C_5H_5Mo(NO)_2Cl$, respectively.

Experimental Section

Microanalyses (Table I) were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany. Infrared spectra (Table II) were taken in potassium bromide pellets or dichloromethane solutions and recorded on a Perkin-Elmer Model 621 spectrometer. Proton nmr spectra (Table I) were taken in chloroform solutions and recorded on a Varian A-60 spectrometer. Ultraviolet and visible spectra were taken in very dilute dichloromethane solutions and recorded on a Cary Model 14 spectrometer. Melting and decomposition points were taken in capillaries and are uncorrected. Molecular weight determinations were carried out by Schwarzkopf Microanalytical Laboratory Woodside, N. Y., using a Mechrolab vapor pressure osmometer in benzene solution.

Thallium cyclopentadienide was prepared from thallium(I) sulfate, potassium hydroxide, and freshly cracked cyclopentadiene by a scaled-up version of the published[8] procedure. Samples purified by sublimation at 130° (0.1 mm) were used. Tetrahydrofuran was freshly distilled over lithium aluminum hydride.

A nitrogen atmosphere was routinely provided for the following three operations: (a) carrying out reactions, (b) handling all filtered solutions of metal complexes, and (c) admission to evacuated vessels.

Preparation of $(C_5H_5)_2Mo(NO)I$.—A mixture of 4.45 g (5 mmoles) of $[C_5H_5Mo(NO)_2I_2]_2$ (prepared from iodine and $C_5H_5Mo(CO)_2NO$ by the published procedure[6]), 2.69 g (10 mmoles) of thallium cyclopentadienide, and 75 ml of tetrahydrofuran was stirred ~18 hr under nitrogen. A yellow precipitate of thallium(I) iodide soon formed. This precipitate was removed by filtration and washed with two 20-ml portions of dichloromethane. Evaporation of the combined tetrahydrofuran filtrate and dichloromethane washings gave black crystals of the crude product. After two recrystallizations from mixtures of dichloromethane and hexane, green-black crystals of $(C_5H_5)_2Mo(NO)I$ were obtained in 64–79% yield (2.5–3.1 g).

Preparation of $(C_5H_5)_2Mo(NO)CH_3$.—A solution of 0.5 g (1.3 mmoles) of $(C_5H_5)_2Mo(NO)I$ in about 20 ml of diethyl ether was treated with 1.0 ml of 3 *M* CH_3MgBr in diethyl ether (3 mmoles) followed by a further 5 ml of diethyl ether. The original brown-green color soon became red. After stirring for ~16 hr the reaction mixture was hydrolyzed with a solution of 2.0 g of ammonium chloride in 10 ml of water. The ether layer was separated and the aqueous layer extracted with a further 25 ml of diethyl ether. The combined brown ether solutions were dried over anhydrous sodium sulfate and filtered from the drying agent. Solvent was removed from the combined filtrates at ~20° (50 mm). The resulting brown crystals were extracted with ~40 ml of boiling hexane in three portions. The filtered extracts were concentrated to ~20 ml and then cooled 2 hr at −10°. The brown crystals were filtered and purified finally by sublimation at 70–80° (0.1 mm) to give 0.085 g (25% yield) of brown crystalline $(C_5H_5)_2Mo(NO)CH_3$.

TABLE II

INFRARED SPECTRUM OF CYCLOPENTADIENYLMOLYBDENUM NITROSYL DERIVATIVES (CM^{-1})

Compound	$\nu(NO)^a$	$\nu(CH)^b$	Other^b
$(C_5H_5)_2Mo(NO)I$	1648 s	3100 w	1410 m, 1360 vw, 1340 vw, 1055 w, 1012 w, 982 w, 920 w, 830 s, 780 s, 593 w, 528 w
$(C_5H_5)_2Mo(NO)CH_3$	1600 s	3095 w, 2960 w, 2880 w	1438 vw, 1410 m, 1359 w, 1340 w, 1155 m, 1053 vw, 1011 m, 995 m, 916 vw, 831 m, 809 s, 765 s, 603 w, 546 w
$C_5H_5Mo(NO)_2Cl$	1759 s, 1665 s	3095 w	1415 w, 1000 w, 915 vw, 886 vw, 845 vw, sh, 817 m, 532 w, 502 vw

[a] Dichloromethane solution. [b] KBr pellet.

Preparation of $C_5H_5Mo(NO)_2Cl$.—Because of its reported[7] hygroscopicity the required $[Mo(NO)_2Cl_2]_n$ was prepared and used immediately as described below.

A mixture of 5.28 g (20 mmoles) of hexacarbonylmolybdenum (obtained from Climax Molybdenum Co., New York, N. Y.) and 200 ml of dichloromethane was treated with excess nitrosyl chloride in several portions. After an initial induction period reaction began accompanied by vigorous gas evolution. A yellow-green precipitate of the product soon formed. After the reaction period was over (*i.e.*, no further changes occurred and addition of more nitrosyl chloride had no effect), the dichloromethane solvent was allowed to evaporate in a stream of nitrogen for several hours. The green solid residue was dried at 25° (0.1 mm) leaving $[Mo(NO)_2Cl_2]_n$.

This green solid was treated with 100 ml of tetrahydrofuran. It dissolved giving a clear green solution with evolution of heat. This solution was treated with 5.4 g (20 mmoles) of thallium cyclopentadienide and the mixture was then stirred overnight (~12 hr) at room temperature. The pure green color became a brown-green.

The resulting reaction mixture was filtered by gravity to remove precipitated thallium chloride formed in the reaction. The precipitate was washed with two 20-ml portions of tetrahydrofuran. Solvent was removed from the combined tetrahydrofuran solutions at ~25° (50 mm) leaving a brown liquid which was dried briefly at 25° (0.1 mm).

The purest sample of the product was obtained by extracting this brown residue with a total of 200 ml of boiling hexane in several portions. After filtering and concentrating to half its

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[6] R. B. King, *Inorg. Chem.*, **6**, 30 (1967).

[7] F. A. Cotton and B. F. G. Johnson, *ibid.*, **3**, 1609 (1964).

[8] F. A. Cotton and L. T. Reynolds, *J. Am. Chem. Soc.*, **80**, 269 (1958).

original volume the hexane solution was cooled overnight at −10°. The resulting yellow-green crystals were filtered and dried to give 0.207 g of pure $C_5H_5Mo(NO)_2Cl$, mp 118–118.5°.

The bulk of the product was obtained from the brown residue after the boiling hexane extraction just described. This residue was extracted with ~150 ml of dichloromethane in four portions. The filtered dichloromethane extracts were treated with 50 ml of hexane and the solvent was removed slowly at 20° (50 mm). Green crystals separated. These were filtered, washed with pentane, dried, and recrystallized from a mixture of dichloromethane and hexane to give 1.059 g of green $C_5H_5Mo(NO)_2Cl$. The total yield was 1.266 g (25% based on $Mo(CO)_6$).

Upon standing at room temperature, samples of $C_5H_5Mo(NO)_2Cl$ evolved nitric oxide. The rate of decomposition appeared to be inversely related to the purity of the sample.

Ultraviolet and Visible Spectra. A. $(C_5H_5)_2Mo(NO)I$.—Gradually increasing absorbance without any maxima in the range 800–220 mμ.

B. $(C_5H_5)_2Mo(NO)CH_3$.—Maxima at 225 mμ (ϵ 4 × 10^4) and 525 mμ (ϵ 4 × 10^2).

C. $C_5H_5Mo(NO)_2Cl$.—Maxima at 222 mμ (ϵ 1.8 × 10^4), 332 mμ (ϵ 2 × 10^3), and 442 mμ (ϵ 8 × 10^2).

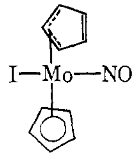
Discussion

The structure of the complex $(C_5H_5)_2Mo(NO)I$ poses an unprecedented problem because of the following points. (1) It is a nonconductor in acetone solution indicating that the iodine is covalently bonded to the molybdenum atom and eliminating the alternative possibility of the iodide salt[9] $[(C_5H_5)_2MoNO]^+I^-$. (2) Its infrared spectrum exhibits a single strong ν(NO) frequency at 1648 cm^{-1} close to the ν(NO) frequencies found in the recently reported[6] compounds $C_5H_5Mo(NO)I_2L$ (L = $(C_6H_5)_3P$, $(C_6H_5O_3)P$, or C_5H_5N) and indicating a normal type of metal nitrosyl ligand. This type of NO ligand is well established to be a three-electron donor.[10] (3) The proton nmr spectrum in the temperature range[11] −55 to +35° exhibits a single sharp resonance in the region normally associated with π-C_5H_5 protons. This demonstrates both the apparent equivalence of the ten cyclopentadienyl protons in this temperature range and the diamagnetism of the complex.

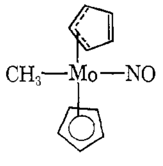
A neutral molybdenum atom requires a total of 12 electrons from the surrounding ligands in order to attain the rare gas configuration expected for a diamagnetic complex. In $(C_5H_5)_2Mo(NO)I$ the molybdenum atom clearly receives one electron from the iodide ligand (point 1 above) and there electrons from the nitrosyl ligand (point 2 above) leaving a total of eight electrons to be received from the two cyclopentadienyl ligands. However, if both of the cyclopentadienyl ligands in $(C_5H_5)_2Mo(NO)I$ are π bonded to the molybdenum atom in the usual manner which involves all five carbon atoms of the ring, they would donate ten rather than eight electrons to the metal atom.

A possible formulation for $(C_5H_5)_2Mo(NO)I$ is I in which one of the cyclopentadienyl rings is bonded to the molybdenum atom in the usual manner where all five carbon atoms are involved but the other cyclopentadienyl ring is bonded to the molybdenum atom as a π-allylic ligand; *i.e.*, only three of the five carbon atoms are bonded to the metal atom leaving an uncomplexed double bond. However, the proton nmr spectrum for $(C_5H_5)_2Mo(NO)I$ with a "fixed" structure I would be expected to exhibit four resonances of relative intensities 5:2:2:1 arising from the one type of protons present in the cyclopentadienyl ring bonded to the metal atom with all five carbon atoms and from the three different types of protons present in the π-allylic cyclopentadienyl ring bonded to the metal atom with only three carbon atoms. Even if the π-allylic cyclopentadienyl ring were rapidly rotating about the metal–ring axis making all of its protons equivalent (an effect now established for $C_8H_8Fe(CO)_3$,[12] $C_5H_5M(CO)_2C_7H_7$ (M = Mo or W),[13] $C_8H_8M(CO)_3$ (M = Cr, Mo, or W),[13,14] $C_8H_8Fe_2(CO)_5$,[15] and (π-C_5H_5)$Fe(CO)_2$(σ-C_5H_5)[16]), the proton nmr spectrum of $(C_5H_5)_2Mo(NO)I$ would still be expected to exhibit two resonances owing to the nonequivalence of the regular π-cyclopentadienyl ring and the π-allylic cyclopentadienyl ring.

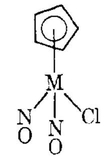
The structure I for $(C_5H_5)_2Mo(NO)I$ and the single resonance for all ten cyclopentadienyl protons in its nmr spectrum can be reconciled by assuming that not only is the π-allylic cyclopentadienyl ring rapidly rotating about the metal–ring axis but also that the cyclopentadienyl ring bonded to the metal atom with all five carbon atoms and the (π-allylic) cyclopentadienyl ring bonded to the metal atom with only three carbon atoms are rapidly exchanging roles with one another. Two phenomena are thus necessary to account for the single cyclopentadienyl resonance in $(C_5H_5)_2Mo(NO)I$. (a) Ring rotation ("ring whizzing") of the π-allylic cyclopentadienyl ring can collapse the four nmr resonances expected for a "fixed" structure I to two nmr resonances. (b) Ring interchange of the two cyclopentadienyl rings can collapse the two nmr resonances arising from ring rotation into the single observed resonance. The inability to change the proton nmr spectrum of $(C_5H_5)_2Mo(NO)I$ upon cooling to −55°



I



II



III

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[9] The solubility of $(C_5H_5)_2Mo(NO)I$ in nonpolar solvents such as benzene and diethyl ether also contraindicates ionic formulations.

[10] It is convenient to consider complexes such as the ones discussed in this paper as formed from neutral metal atoms and neutral ligands. For a general discussion of an appropriate formal system for organizing coordination chemistry and a precise definition of the number of electrons donated by various ligands see R. B. King, Advances in Chemistry Series, No. 62, American Chemical Society, Washington, D. C., 1967, p 203.

[11] This spectrum was studied on a Varian HA-100 spectrometer equipped with a low-temperature probe. The author is indebted to Mr. J. F. Whidby for experimental assistance in using this spectrometer.

[12] F. A. Cotton, A. Davison, and J. W. Faller, *J. Am. Chem. Soc.*, **88**, 4570 (1966); C. E. Keller, B. A. Shoulders, and R. Pettit, *ibid.*, **88**, 4760 (1966); F. A. L. Anet, H. D. Kaesz, A. Maasbol, and S. Winstein, *ibid.*, **89**, 2489 (1967).

[13] R. B. King, *J. Organometal. Chem.* (Amsterdam), **8**, 129 (1967).

[14] C. G. Kreiter, A. Maasbol, F. A. L. Anet, H. D. Kaesz, and S. Winstein, *J. Am. Chem. Soc.*, **88**, 3444 (1966).

[15] C. E. Keller, G. F. Emerson, and R. Pettit, *ibid.*, **87**, 1389 (1965).

[16] M. J. Bennett, Jr., F. A. Cotton, A. Davison, J. W. Faller, S. J. Lippard, and S. M. Morehouse, *ibid.*, **88**, 4371 (1966).

suggests that ring interchange is very difficult to slow down by cooling.

The new compound $(C_5H_5)_2Mo(NO)I$ is an air-stable green-black solid which sublimes at 130° (0.1 mm) with extensive decomposition. In attempts to prepare related compounds, a few reactions of $(C_5H_5)_2Mo(NO)I$ were investigated. The reaction with methylmagnesium bromide was particularly interesting since it yielded a volatile brown solid shown to be the closely related methyl derivative $(C_5H_5)_2Mo(NO)CH_3$ (II). The proton nmr spectrum of II exhibits two singlet resonances at τ 4.24 and 8.94 arising from ten apparently equivalent cyclopentadienyl protons and three equivalent methyl protons, respectively. The position of the methyl resonance is reasonable for a methyl group directly bonded to the molybdenum atom. The preparation of $(C_5H_5)_2Mo(NO)CH_3$ from $(C_5H_5)_2Mo(NO)I$ demonstrates the possibility of converting one $(C_5H_5)_2Mo(NO)Y$ compound into another $(C_5H_5)_2Mo(NO)Y'$ compound without destroying or modifying the two cyclopentadienyl ligands and the nitrosyl group.

In 1957[17] the chromium compound $C_5H_5Cr(NO)_2Cl$ (III, M = Cr) was first reported. Subsequently, this compound has been a useful intermediate for the synthesis of other cyclopentadienylchromium nitrosyl derivatives including the alkyls $C_5H_5Cr(NO)_2R$ (R = CH_3, C_2H_5, σ-C_5H_5, etc.),[18] the cation[19] $[C_5H_5Cr(NO)_2CO]^+$, and the dimeric compound $[C_5H_5Cr(NO)_2]_2$ with bridging nitrosyl groups.[20] Despite the gap of over 12 years and the demonstrated synthetic value of compounds of the type $C_5H_5M(NO)_2Cl$, the molybdenum and tungsten analogs (III, M = Mo or W) have not yet been reported.

The reaction between the polymeric[3] $[Mo(NO)_2Cl_2]_n$ and thallium cyclopentadienide has now been found to provide the first synthetic route to the missing $C_5H_5Mo(NO)_2Cl$. The most noteworthy property of this new molybdenum compound is its instability compared with its chromium analog. Upon standing, samples of $C_5H_5Mo(NO)_2Cl$ soon darken with evolution of nitric oxide. The instability of $C_5H_5Mo(NO)_2Cl$ relative to its chromium analog $C_5H_5Cr(NO)_2Cl$ may arise from similar causes to the instability of the palladium compound[21] C_5H_5PdNO relative to its nickel analog C_5H_5NiNO. Apparently second-row (4d) transition metals form weaker bonds with nitric oxide than first-row (3d) transition metals. Carbon monoxide has already been observed to form weaker bonds with second-row (4d) transition metals than with first-row (3d) transition metals;[22] *e.g.*, molybdenum carbonyl derivatives appear to lose carbon monoxide more readily than their chromium analogs.

The relative instability of $C_5H_5Mo(NO)_2Cl$ and related compounds compared with their chromium analogs has limited attempts to synthesize other $C_5H_5Mo(NO)_2$ derivatives. In attempts to prepare $[C_5H_5Mo(NO)_2]_2$ and $C_5H_5Mo(NO)_2CH_3$, the chloride $C_5H_5Mo(NO)_2Cl$ was treated with sodium borohydride in a two-phase water-benzene system and with methylmagnesium bromide in diethyl ether solution using conditions similar to those effective for preparing analogous chromium compounds. In both cases reactions occurred, but no cyclopentadienylmolybdenum nitrosyl derivatives could be isolated from the reaction mixtures. Apparently the reaction conditions decompose the products.

Reactions between thallium cyclopentadienide and other transition metal halides have been investigated but have proved to be of less value for synthesis of new compounds than the reactions described in this paper. The heptafluoropropyliron derivative $C_3F_7Fe(CO)_4I$ reacts rapidly with thallium cyclopentadienide to give the known compound $C_3F_7Fe(CO)_2C_5H_5$ previously[23] obtained by photochemical decarbonylation of $C_3F_7COFe(CO)_2C_5H_5$. The halides $C_5H_5Fe(CO)_2I$ and $C_7H_7Mo(CO)_2I$ which react readily with sodium cyclopentadienide giving $C_5H_5Fe(CO)_2C_5H_5$[18] and $C_5H_5Mo(CO)_2C_7H_7$,[24] respectively, appear not to react with thallium cyclopentadienide in tetrahydrofuran at room temperature. The π-allyl derivative $C_3H_5Fe(CO)_3I$[25] gives $[C_5H_5Fe(CO)_2]_2$ upon reaction with thallium cyclopentadienide. The cobalt complex $C_5H_5Co(CO)I_2$[26] gives the cation $[(C_5H_5)_2Co]^+$ upon treatment with thallium cyclopentadienide.

Qualitative observations of reactions of these and other halides with thallium cyclopentadienide indicate the following series of reactivity toward this reagent of metal iodides[27] containing carbonyl and π-cyclopentadienyl groups: $C_3F_7Fe(CO)_4I$ (most reactive) > $[C_5H_5Mo(NO)I_2]_2$, $C_5H_5Co(CO)I_2$ > $C_3H_5Fe(CO)_3I$ > $C_5H_5Fe(CO)_2I$, $C_7H_7Mo(CO)_2I$ (least reactive). From these data additional iodide and C_3F_7 ligands appear to increase the reactivity whereas a π-C_5H_5 ligand appears to decrease the reactivity of the metal iodide complexes. This is consistent with the reactivity of these metal iodide complexes being determined by the amount of retrodative $d\pi$–$d\pi$ bonding between the metal atom and the iodide ligand. Increased retrodative $d\pi$–$d\pi$ bonding increases the strength of the metal–iodine bond and hence decreases the reactivity of the metal iodide derivative. Introduction of more iodide ligands (*i.e.*, in proceeding from $C_5H_5Fe(CO)_2I$ to $C_5H_5CoCOI_2$) increases the formal oxidation state of the metal atom thereby decreasing its d-electron density available for retrodative $d\pi$–$d\pi$ bonding. Replacement of carbonyl groups with the less strongly retro-

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(17) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **2**, 38 (1956).

(18) T. S. Piper and G. Wilkinson, *ibid.*, **3**, 104 (1956).

(19) E. O. Fischer and P. Kuzel, *Z. Anorg. Allgem. Chem.*, **317**, 226 (1962).

(20) R. B. King and M. B. Bisnette, *Inorg. Chem.*, **3**, 791 (1964).

(21) E. O. Fischer and A. Vogler, *Z. Naturforsch.*, **18b**, 771 (1963).

(22) See ref 13 and references cited therein.

(23) R. B. King and M. B. Bisnette, *J. Organometal. Chem.* (Amsterdam), **2**, 15 (1964).

(24) R. B. King and M. B. Bisnette, *Inorg. Chem.*, **3**, 785 (1964).

(25) R. A. Plowman and F. G. A. Stone, *Z. Naturforsch.*, **17b**, 575 (1962).

(26) R. B. King, *Inorg. Chem.*, **5**, 82 (1966).

(27) Such a comparison appears meaningful only when made with metal derivatives containing the same halogen. For this reason, comparison is made only with the metal iodide derivatives studied.

dative bonding ("back bonding") π-C_5H_5 or π-C_7H_7 ligand increases the density of d electrons on the metal atom available for retrodative dπ–dπ bonding with the iodine atom.

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The Far-Infrared Spectra of Some Group IV–Transition Metal Carbonyl Compounds

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The far-infrared spectra (100–550 cm^{-1}) of 18 compounds containing tin–transition metal bonds are presented. It is shown that reasonable assignments can be made of absorptions largely due to metal–metal vibrations. Moreover, variations in the frequencies of these absorptions can be correlated with variations in the frequencies of the transition metal carbonyl absorptions (1900–2200-cm^{-1} region). This correlation can be interpreted in terms of the π-accepting properties of the R_3Sn moiety and hence is related to the nature of R.

Introduction

We wish to report the far-infrared spectra (100–550 cm^{-1}) for some 18 compounds, of which five are new, containing a tin–transition metal bond. The purpose of this work has been threefold. Primarily, we have sought to obtain information for a region of the infrared that has been only briefly studied. Secondly, we wished to determine whether such a technique could be used satisfactorily to provide a reasonable assignment of the metal–metal stretching vibrations. Thirdly, we were also interested in determining whether the frequencies of the metal–metal stretching vibrations displayed a variation consistent with the shifts observed in the carbonyl stretching region for a given series of compounds. Thus, Graham, *et al.*,[1] have shown for a large number of group IV metal–transition metal compounds that the carbonyl stretching frequencies are sensitive to the nature of the ligands attached to the group IV metal. They have postulated that some form of dπ–dπ interaction may occur between the group IV metal and the transition metal and that the former acts as the π acceptor. Such an interaction, we felt, might be susceptible to observation in the metal–metal stretching vibrations, provided a reasonable series of compounds could be studied. We have examined the two distinct series of compounds $(CH_3)_{3-n}Cl_nSn$–M, where M is $Mn(CO)_5$ and $Mo(CO)_3(\pi$-$C_5H_5)$, respectively. In addition, we have examined the series $(CH_3)_2XSnMn(CO)_5$, where X = CF_3, (Cl), Br, and I, which may provide some information on the nature of this interaction. Finally, we have examined the far-infrared spectra of the additional metal–metal bonded compounds $R_3SnFe(CO)_2(\pi$-$C_5H_5)$ (where R = CH_3 or C_6H_5), $(CH_3)_3SnW(CO)_3(\pi$-$C_5H_5)$, $(CH_3)_2ClSnW(CO)_3(\pi$-$C_5H_5)$, and $(CH_3)_3SnCo(CO)_4$, which allow further useful comparisons to be made.

Experimental Section

Preparation of Starting Materials.—The preparations of $(CH_3)_3SnMn(CO)_5$, $(C_6H_5)_3SnMn(CO)_5$, $Cl_3SnMn(CO)_5$, $(CH_3)_3SnCo(CO)_4$, and $(CH_3)_3SnFe(CO)_2(\pi$-$C_5H_5)$ were described by Gorsich.[2] The preparations of $(CH_3)_3SnMo(CO)_3(\pi$-$C_5H_5)$, $(C_6H_5)_3SnMo(CO)_3(\pi$-$C_5H_5)$, and $(CH_3)_3SnW(CO)_3(\pi$-$C_5H_5)$ were as described by Graham.[1a] The preparations of $Cl(CH_3)_2SnMn(CO)_5$, $Cl_2(CH_3)SnMn(CO)_5$, $Cl(CH_3)_2SnW(CO)_3(\pi$-$C_5H_5)$, $Cl(CH_3)_2SnMo(CO)_3(\pi$-$C_5H_5)$, $Cl_2CH_3SnMo(CO)_3(\pi$-$C_5H_5)$, $Cl_3SnMo(CO)_3(\pi$-$C_5H_5)$, $Br(CH_3)_2SnMn(CO)_5$, $I(CH_3)_2SnMn(CO)_5$, and $CF_3(CH_3)_2SnMn(CO)_5$ will be described elsewhere.

Recording of Spectra.—The spectra in the carbonyl stretching region were recorded as solutions in cyclohexane, using 0.1-mm NaCl solution cells, on a Beckman IR-7 spectrometer. Calibration was made using the water line at 1942.5 cm^{-1}. The spectra for the 70–350-cm^{-1} region were recorded on a Beckman IR-11 spectrometer; 1.5-mm propathene plates were used as windows and the samples were made up in Nujol as thick pastes. Nujol in propathene possesses a weak peak at 170 cm^{-1} and a medium weak band at 250 cm^{-1}. Calibration was made using the water line at 203.6 cm^{-1}. The remaining region 350–3000 cm^{-1} was recorded on a Beckman IR-10 spectrometer. Cesium iodide windows were used and the spectra were calibrated with the characterisic bands in polystyrene.

Results

(A) $(CH_3)_{3-n}Cl_nSnMn(CO)_5$, Where n = 0, 1, 2, 3.—In Figure 1 are reproduced the spectra for the region 300–140 cm^{-1}, of the series $(CH_3)_{3-n}Cl_nSnMn(CO)_5$, where n = 0, 1, 2, 3, and the data are tabulated in Table I for the region 550–100 cm^{-1}. Clearly, one obvious common feature is the medium to strong intensity band in the 175–205-cm^{-1} region. The band at 182 cm^{-1} in the spectrum of $(CH_3)_3SnMn(CO)_5$ is close to the band at 180 cm^{-1} that appears in the Raman spectrum of the same compound and which has been associated with the Sn–Mn stretching vibra-

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(2) R. D. Gorsich, *J. Am. Chem. Soc.*, **84**, 2486 (1962).