characteristics of the substituents have been attempted: Hammett σ_P constants,[4] substituent electronegativities from ν_{PO} bond vibrations,[5] empirically derived mutually consistent group electronegativities using various data,[5] Hammett σ_I constants,[6] and substituent steric requirements. The advantages and disadvantages of these materials in looking for such correlation phenomena have been recently considered in some detail.[7,8]

We find only a weak positive correlation of the IS with the substituent electronegativities indicating a slightly increasing total s-electron density at the tin nucleus with increasing electron-withdrawing capacity of the para substituent. In addition, we find some correlation of the IS with the QS as the magnitude of the observed splitting generally decreases with increasing shift values.[7] Such behavior is consistent with slightly decreasing coordination abilities of the nitrogen atoms toward the central tin atom.[9] Both of the above correlations would be consistent with the conclusion that the degree of coordination between the tin and the nitrogens in these compounds varies due to the inductive transmittal of electronic effects from the phenyl para positions. One might thus expect to find a slightly larger central hole in the F-substituted compound than in the parent Cl_2SnTPP. Unfortunately, only the structure of the latter has been reported.[10]

All seven compounds studied here exhibit distinct asymmetries in their doublet Mossbauer spectra. The ratio of the high-energy wing area to the low-energy wing is indicated for each sample spectrum in Table I. It is quite apparent that increased area asymmetries are accompanied by decreased splittings. Such asymmetry variations (if indeed due to variations in the bonding environment of the tin) should represent variations in the spatial anisotropy of the recoil-free fraction of the tin atoms.[11] One might expect the tin to be more tightly bound in the "plane" roughly defined by the nitrogen atoms rather than along the Cl–Sn–Cl axis. All of the Mossbauer measurements were obtained with finely powdered samples but, because nonrandom orientations of the microcrystals could also lead to spectral asymmetries, several of the compounds were repeatedly reground and reexamined. No significant changes in the doublet asymmetries were observed, thus indicating a random orientation of the polycrystalline absorbers.

Possible line shape model errors in the spectrum-fitting routine have been considered and we are quite confident that they are negligible in the determination of the IS and QS from these well-fitted spectra. The distribution of the calculated residuals is uniform across the absorption peak of each spectrum. The supposed quadrupolar-split spectra may, however, actually be the result of two very closely spaced singlets originating from two crystal forms of each compound; the two forms differ, perhaps, by the orientations of the phenyl groups. We have no evidence to support such a supposition and these data indicate that both crystal forms would be equally prevalent, which on stereochemical considerations of the possible structures would be unlikely. Careful analyses of these spectra in a strong external magnetic field would, however, differentiate between a genuine doublet and two closely spaced singlets. Chemical impurities at a 50% level are known not to be significant in these chromatographically purified and analytically characterized compounds.[2]

We conclude, therefore, that though all of these complexes exhibit discernible doublet ^{119m}Sn Mossbauer spectra with various magnitudes of the splitting, the causes are not completely clear. The doublets might be two singlets, closely spaced and representing two structural forms of the complexes, although we consider this unlikely. Differences in the crystal packing arrangements of these solid-state complexes might also yield variations in the electric field gradient (EFG) at the tin nuclear site, but such sensitivity of the EFG to long-range interactions would be highly unusual for such molecular solids. As a further consideration, we have estimated the effect of slight movements of the tin atom along the Cl–Sn–Cl axis on the basis of the point-charge model[12] and found that if the atom were to pop out of the central hole by up to 0.2 Å, then the QS might be expected to vary by about 10–15%, as observed. The effect of such a distortion upon the IS would probably be very small as the accompanying rehybridization of the tin bonding orbitals would not substantially affect the total s-electron density at the tin nucleus. However, an independent test (and confirmation) of this explanation of the data requires further X-ray structural analyses of some of the substituted complexes.

Acknowledgment. Portions of this work were carried out while N. D. was a National Research Council–National Bureau of Standards Postdoctoral Research Associate and this support is gratefully acknowledged.

Registry No. $Cl_2SnT(p\text{-}i\text{-}C_3H_7)PP$, 52628-87-2; $Cl_2SnT(p\text{-}CH_3)PP$, 26334-83-8; Cl_2SnTPP, 26334-85-0; $Cl_2SnT(p\text{-}OCH_3)PP$, 26334-82-7; $Cl_2SnT(p\text{-}Br)PP$, 52628-86-1; $Cl_2SnT(p\text{-}Cl)PP$, 26334-84-9; $Cl_2SnT(p\text{-}F)PP$, 52628-88-3.

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

Some Studies on Tungsten Carbonyl Nitrosyl Derivatives

R. B. King,* M. S. Saran,[1] and S. P. Anand[2]

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Cleavage of the metal–metal bond in bimetallic metal carbonyl derivatives such as $[C_5H_5M(CO)_3]_2$ (M = Mo, W), $M_2(CO)_{10}$ (M = Mn, Re), and $[C_5H_5M(CO)_2]_2$ (M = Fe, Ru) by reagents such as halogens and alkali metals provides useful routes to interesting monometallic transition metal derivatives.[3] In this connection, the recently reported[4] unsymmetrical bimetallic tungsten carbonyl nitrosyl hydride

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[1] Postdoctoral research associate, 1969–1974.

[2] Postdoctoral research associate, 1973–1974.

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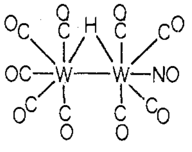
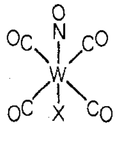
$HW_2(CO)_9NO$ (I) was of interest since similar tungsten–tungsten bond cleavage reactions could give $W(CO)_4(NO)X$ derivatives isoelectronic with the well-known[3] $M(CO)_5X$ (M = Mn, Tc, Re) derivatives.

These considerations led to an investigation of the reactions of $HW_2(CO)_9NO$ with sodium amalgam and with halogenating reagents such as nitrosyl chloride and iodine. In our hands, reactions of $HW_2(CO)_9NO$ with sodium amalgam in tetrahydrofuran solution followed by addition of methyl iodide or trimethyltin chloride gave only traces of yellow rather intractable products without the ν(NO) frequency in their infrared spectra expected for a $RW(CO)_4NO$ derivative. However, halogenations of $HW_2(CO)_9NO$ with nitrosyl chloride and with iodine provided novel synthetic routes to the halides *trans*-$W(CO)_4(NO)X$ (II, X = Cl, I).

After our work on the syntheses of the *trans*-$W(CO)_4(NO)X$ halides from $HW_2(CO)_9NO$ was essentially completed, a report by Barraclough, Bowden, Colton, and Commons[5] on the syntheses of the same *trans*-$W(CO)_4(NO)X$ halides by nitrosation of $[(C_2H_5)_4N][W(CO)_5X]$ became available to us. We have therefore phased out our work in this area. This note reports our syntheses of *trans*-$W(CO)_4(NO)X$ (II, X = Cl, I) from $HW_2(CO)_9NO$ as well as some reactions of *trans*-$W(CO)_4(NO)I$ which are not discussed in recent papers by Colton and Commons.[6,7]



I



II

Experimental Section

Commercial hexacarbonyltungsten (Pressure Chemical Corp., Pittsburgh, Pa.), after resublimation, was converted to $HW_2(CO)_9NO$ by reaction with $NaBH_4$ in tetrahydrofuran to give $Na[HW_2(CO)_{10}]$ followed by nitrosation of this sodium salt with sodium nitrite and phosphoric acid in aqueous solution.[4,8] From 50 g (142 mmol) of $W(CO)_6$ this procedure gave 17 g (37% yield) of $HW_2(CO)_9NO$ after crystallization from dichloromethane and heating at ~45° (1 mm) to remove any unreacted $W(CO)_6$. *tert*-Butyl isocyanide was prepared from *tert*-butylamine *via tert*-butylformamide.[9] Other aspects of the experimental procedures are similar to those described in previous papers from this laboratory.[10]

Reaction of $HW_2(CO)_9NO$ with Nitrosyl Chloride. Nitrosyl chloride was passed for 10 min through a solution of 0.73 g (1.12 mmol) of $HW_2(CO)_9NO$ in 75 ml of benzene. The color changed from red-orange to brown and a yellow precipitate separated. Removal of solvent at ~25° (35 mm) followed by sublimation at 45–50° (1.5 mm) gave a 35% yield of a yellow sublimate of *trans*-$W(CO)_4(NO)Cl$ identified by molecular weight and elemental analyses (C, N, Cl, O, W) and by comparison of its infrared spectrum in the ν(CO) region with that reported in the literature.[5]

Reaction of $HW_2(CO)_9NO$ with Iodine. A solution of 11.0 g (16.9 mmol) of $HW_2(CO)_9NO$ in 400 ml of dichloromethane was treated dropwise with a solution of 7.0 g (27.6 mmol as I_2) of iodine in 250 ml of dichloromethane. The filtered dichloromethane solution was concentrated nearly to dryness and then chromatographed on a 3 × 50 cm Florisil column. A small amount of $W(CO)_6$ was first eluted with pure hexane. The major yellow band of *trans*-$W(CO)_4(NO)I$ was eluted with 1:9 dichloromethane–hexane. Evaporation of this eluate gave 5.4 g (70% yield based on available nitrosyl groups) of *trans*-$W(CO)_4(NO)I$, identified by molecular weight and elemental analyses (C, N, I, O, W) and comparison of its infrared spectrum in the ν(CO) region with that reported in the literature.[5]

Reactions of *trans*-$W(CO)_4(NO)I$ with *tert*-Butyl Isocyanide. (a) Hexane at Room Temperature. A mixture of 0.453 g (1 mmol) of *trans*-$W(CO)_4(NO)I$, 1 ml (0.72 g, 8.7 mmol) of *tert*-butyl isocyanide, and 60 ml of hexane was stirred for 18 hr at room temperature. A brown solid separated during the course of this reaction. Dichloromethane (25 ml) was added to dissolve this brown solid. Filtration and concentration of the filtrate to ~25 ml at ~25° (35 mm) gave 0.32 g (57% yield) of *cis*-$(Me_3CNC)_2W(CO)_2(NO)I$.

(b) Boiling Benzene (80°). A mixture of 0.453 g (1 mmol) of *trans*-$W(CO)_4(NO)I$, 1 ml (0.72 g, 8.7 mmol) of *tert*-butyl isocyanide, and 60 ml of benzene was boiled under reflux for 2.5 hr. Removal of benzene at 25° (35 mm) was followed by chromatography on a 2.5 × 35 cm Florisil column to give 0.27 g (48% yield) of *cis*-$(Me_3CNC)_2W(CO)_2(NO)I$, eluted with 2:3 dichloromethane–hexane, followed by 0.14 g (23% yield) of $(Me_3CNC)_3W(CO)(NO)I$, eluted with pure dichloromethane.

(c) Boiling Toluene (110°). A mixture of 0.453 g (1 mmol) of *trans*-$W(CO)_4(NO)I$, 1.5 ml (1.08 g, 13.0 mmol) of *tert*-butyl isocyanide, and 60 ml of toluene was boiled under reflux for 17 hr. Chromatography on a 2.5 × 35 cm Florisil column gave 0.28 g (42% yield) of bright yellow $(Me_3CNC)_4W(NO)I$.

Properties of the $(Me_3CNC)_nW(CO)_{4-n}(NO)I$ Derivatives. (a) *cis*-$(Me_3CNC)_2W(CO)_2(NO)I$: yellow to orange, mp 139–140°. Infrared spectrum (CH_2Cl_2): ν(CN) 2201 (m) and 2182 (m) cm^{-1}; ν(CO) 2040 (s) and 1976 (s) cm^{-1}; ν(NO) 1642 (s) cm^{-1}. Proton nmr ($CDCl_3$): τ 8.43. *Anal.* Calcd for $C_{12}H_{18}IN_3O_3W$: C, 25.6; H, 3.2; N, 7.4; O, 8.5. Found: C, 25.3; H, 3.3; N, 7.4; O, 9.2.

(b) $(Me_3CNC)_3W(CO)(NO)I$: yellow, dec pt 166°. Infrared spectrum (CH_2Cl_2): ν(CN) 2189 (w) and 2139 (s) cm^{-1}; ν(CO) 1961 (s) cm^{-1}; ν(NO) 1602 (s) cm^{-1}. Proton nmr ($CDCl_3$): τ 8.44. *Anal.* Calcd for $C_{16}H_{27}IN_4O_2W$: C, 31.1; H, 4.4; N, 9.1; O, 5.2. Found: C, 30.9; H, 4.2; N, 8.9; O, 5.8.

(c) *trans*-$(Me_3CNC)_4W(NO)I$: bright yellow, dec pt >185°. Infrared spectrum (CH_2Cl_2): ν(CN) 2112 (s) and 2070 (w, sh) cm^{-1}; no ν(CO); ν(NO) 1564 (m) cm^{-1}. Proton nmr ($CDCl_3$): τ 8.49. *Anal.* Calcd for $C_{20}H_{36}IN_5OW$: C, 35.7; H, 5.4; N, 10.4; O, 2.4. Found: C, 34.8; H, 5.3; N, 10.1; O, 2.8.

Preparation of $[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]W(CO)_2(NO)I$. Reaction of 0.453 g (1 mmol) of *trans*-$W(CO)_4(NO)I$ and 0.9 g (2 mmol) of $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ in 70 ml of boiling hexane for 1 hr followed by chromatography on Florisil in hexane solution gave after elution with dichloromethane 0.72 g (91% yield) of yellow $[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]W(CO)_2(NO)I$, mp 182–183° dec. Infrared spectrum (CH_2Cl_2): ν(CO) 2030 (s) and 1950 (s) cm^{-1}; ν(NO) 1630 (m) cm^{-1}. *Anal.* Calcd for $C_{28}H_{24}INO_3P_2W$: C, 42.3; H, 3.0; I, 16.0; N, 1.8; O, 6.0. Found: C, 42.7; H, 3.3; I, 17.3; N, 1.7; O, 6.1.

Conversion of *trans*-$W(CO)_4(NO)I$ to $C_5H_5W(CO)_2NO$. A mixture of 0.906 g (2 mmol) of *trans*-$W(CO)_4(NO)I$, 0.538 g (2 mmol) of thallium cyclopentadienide, and 75 ml of tetrahydrofuran was boiled under reflux for 75 min. Tetrahydrofuran was then removed at ~25° (35 mm). A solution of the residue in 100 ml of hexane was chromatographed on a 2.5 × 35 cm Florisil column. Elution of the yellow band with hexane followed by concentration of the hexane eluate to ~10 ml and cooling to 0° gave 0.41 g (61% yield) of yellow-orange crystalline $C_5H_5W(CO)_2NO$, mp 106–107° (lit.[11] mp 105–107°), identified by its infrared ν(CO) and ν(NO) frequencies.

Use of sodium cyclopentadienide instead of thallium cyclopentadienide in the above reaction also gave $C_5H_5W(CO)_2NO$, but only in ~22% yield. Similar reactions of *trans*-$W(CO)_4(NO)I$ with phenyllithium in benzene, methyllithium in diethyl ether, allylmagnesium chloride in tetrahydrofuran, and $K_2C_8H_8$ in tetrahydrofuran on a 1-mmol scale all gave negative results or intractable mixtures apparently not containing the desired organotungsten compounds.

Discussion

The formation of *trans*-$W(CO)_4(NO)Cl$ from the reaction of $HW_2(CO)_9NO$ with nitrosyl chloride is rather unexpected since a similar reaction of $W(CO)_6$ with nitrosyl chloride gives the carbonyl-free complex $[W(NO)_2Cl_2]_n$.[12] This observation suggests that nitrosyl chloride only functions as a chlorinating agent in its reaction with $HW_2(CO)_9NO$, which already

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(9) I. Ugi and R. Meyr, *Chem. Ber.*, **93**, 239 (1960).

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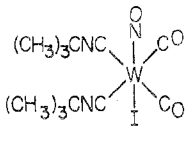
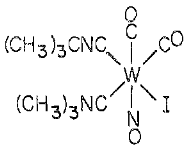
has the necessary nitrosyl group to form *trans*-$W(CO)_4(NO)Cl$, whereas nitrosyl chloride must also function as a nitrosylating agent in its reaction with $W(CO)_6$. This dichotomy in the action of nitrosyl chloride on transition metal systems can account for the very different pathways in its reactions with $W(CO)_6$ and $HW_2(CO)_9NO$.

The tendency for $HW_2(CO)_9NO$ to form halides of the type *trans*-$W(CO)_4(NO)X$ with halogenating agents is also demonstrated by the reaction of $HW_2(CO)_9NO$ with elemental iodine to give *trans*-$W(CO)_4(NO)I$ in yields up to 70% based on available nitrosyl groups. Since only one of the two tungsten atoms in $HW_2(CO)_9NO$ has a nitrosyl group, halogenation of $HW_2(CO)_9NO$ must also lead to other tungsten complexes from the tungsten atom without the nitrosyl group. These tungsten by-products can complicate the separation of pure *trans*-$W(CO)_4(NO)X$ derivatives from the halogenation of $HW_2(CO)_9NO$. In the preparation of *trans*-$W(CO)_4(NO)I$ from $HW_2(CO)_9NO$ and iodine, separation of a pure product is facilitated if excess iodine is used. The remaining tungsten products from this preparation can appear as brown solids insoluble in dichloromethane or as a brown, very strongly adsorbed band on the chromatography column after removal of the *trans*-$W(CO)_4(NO)I$. The iodination of $HW_2(CO)_9NO$ in benzene, furthermore, can give erratic yields of a blue volatile solid of stoichiometry $[W(CO)_4I]_n$; the nature of this product is uncertain. Reaction of $HW_2(CO)_9NO$ with bromine has been shown spectroscopically to produce *trans*-$W(CO)_4(NO)Br$, but a reliable procedure has not been found for separating pure *trans*-$W(CO)_4(NO)Br$ from the $W(CO)_6$ concurrently produced in this reaction.

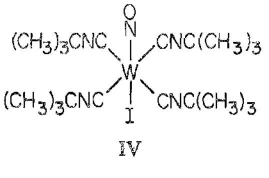
Colton and Commons have reported some reactions of *trans*-$W(CO)_4(NO)X$ ($X = Cl, Br, I$) with simple tertiary phosphines and arsines[6] to give either monosubstituted *mer*-$W(CO)_3L(NO)X$ or disubstituted *cis*-$W(CO)_2L_2(NO)X$ ($L = (C_6H_5)_3P, (C_6H_5)_3As$; $X = Cl, Br, I$) depending upon the severity of the reaction conditions. We have found conditions for the reaction of *trans*-$W(CO)_4(NO)I$ with *tert*-butyl isocyanide where the dicarbonyl *cis*-$(Me_3CNC)_2W(CO)_2(NO)I$, the monocarbonyl $(Me_3CNC)_3W(CO)(NO)I$, or even the carbonyl-free *trans*-$(Me_3CNC)_4W(NO)I$ can be obtained simply by varying the reaction temperature from room temperature to 110°. Stereochemistries of *cis*-$(Me_3CNC)_2W(CO)_2(NO)I$ with the pairs of both the carbonyl and *tert*-butyl isocyanide ligands in relative cis positions (*i.e.*, IIIa or IIIb) and of *trans*-$(Me_3CNC)_4W(NO)I$ with the nitrosyl and iodide ligands in trans positions (*i.e.*, IV with local C_{4v} symmetry) are supported by the observed numbers and positions of $\nu(CN)$ and $\nu(CO)$ frequencies, but the available infrared data do not allow either a decision between IIIa and IIIb for the disubstituted derivative or an unequivocal elucidation of the stereochemistry of the trisubstituted derivative $(Me_3CNC)_3W(CO)(NO)I$. However, structure IIIa seems more probable than IIIb for the disubstituted *cis*-$(Me_3CNC)_2W(CO)_2(NO)I$ in view of its single, sharp *tert*-butyl proton nmr resonance and its formation from *trans*-$W(CO)_4(NO)I$. In *cis*-$(Me_3CNC)_2W(CO)_2(NO)I$ the two $\nu(CO)$ frequencies are separated by 64 cm^{-1} whereas the two $\nu(CN)$ frequencies are separated by only 19 cm^{-1} indicating that the stretch–stretch interaction constants are appreciably smaller for the *tert*-butyl isocyanide ligands than for the carbonyl ligands in accord with previous observations[13] on octahedral *tert*-butyl isocyanide metal carbonyl complexes, particularly those of the type *fac*-$(Me_3CNC)_3M(CO)_3$ ($M = Cr, Mo, W$). In the series $(Me_3CNC)_nW(CO)_{4-n}(NO)I$ ($n = 2$–4) the position of the $\nu(NO)$ frequency decreases by ~40 cm^{-1} upon each successive substitution of a carbonyl group with a *tert*-butyl isocyanide ligand in accord with expectations based on the weaker π-acceptor ability of *tert*-butyl isocyanide relative to carbon monoxide.[14]



IIIa



IIIb



IV

Colton and Commons[7] have also reported some *cis*-(bidentate)$W(CO)_2(NO)X$ complexes from the ligands $(C_6H_5)_2ECH_2E(C_6H_5)_2$ ($E = P$ or As) with methano bridges. We have prepared the closely related complex *cis*-$[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]W(CO)_2(NO)I$; the analogous chloride was previously prepared by a different method.[15]

Reactions of *trans*-$W(CO)_4(NO)I$ with appropriate reactive organometallics could provide a route to novel organotungsten carbonyl nitrosyls. Thus *trans*-$W(CO)_4(NO)I$ reacts with thallium cyclopentadienide or, less efficiently, sodium cyclopentadienide to give the known[11] $C_5H_5W(CO)_2NO$, but this preparation of $C_5H_5W(CO)_2NO$ is less convenient than those currently in use. Unfortunately, attempts to make more interesting organotungsten carbonyl nitrosyls by variations of this method as described in the Experimental Section led to uniformly negative results.

Acknowledgment. We are indebted to the National Cancer Institute for partial support of this work under Grant CA-12938-02.

Registry No. *cis*-$(Me_3CNC)_2W(CO)_2(NO)I$, 52699-24-8; $(Me_3CNC)_3W(CO)(NO)I$, 52699-25-9; *trans*-$(Me_3CNC)_4W(NO)I$, 52699-26-0; $[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]W(CO)_2(NO)I$, 51132-29-7; *trans*-$W(CO)_4(NO)I$, 39899-82-6; $HW_2(CO)_9NO$, 52699-27-1.

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Contribution No. 2525 from the Department of Chemistry,
Indiana University, Bloomington, Indiana 47401

Studies of Boranes. XLI.[1] A New Boron Hydride, Tridecaborane(19)

Jerome Rathke, David C. Moody, and Riley Schaeffer*

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In this paper the synthesis and properties of $B_{13}H_{19}$ and attempts to identify intermediates in its formation are reported. A brief report of X-ray crystal structure of this compound has already appeared.[2]

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(1) For the preceding paper see J. Rathke and R. Schaeffer, *Inorg. Chem.*, 13, 760 (1974).

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