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ORGANOMETALLIC COMPOUNDS HAVING METAL—METAL BONDS

XXV*. TETRACARBONYLNITROSYL-MOLYBDENUM AND -TUNGSTEN DERIVATIVES OF THE GROUP IV ELEMENTS

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Summary

Tetraethylammonium salts of the anions $[R_3M'M(CO)_5]^-$ react with $NO^+PF_6^-$ to form the yellow to orange-red air stable products $R_3M'M(CO)_4NO$ (M = Mo, R_3M' = $GePh_3$, $SnPh_3$, $SnMe_3$, $PbPh_3$; M = W, R_3M' = $SiPh_3$, $SiPh_2Me$, $GePh_3$, $SnPh_3$, $SnMe_3$, $PbPh_3$). Yields vary from 7 to 54% and M = Cr derivatives could not be obtained. Alternative synthetic procedures for the known complexes $XW(CO)_4NO$ (X = Cl, Br, I) are described. IR spectroscopy established that the compounds exist as *trans* isomers in all cases. On the basis of carbonyl stretching force constants and NMR coupling constants, some qualitative comments are made on the bonding in the isoelectronic series $[Me_3SnW(CO)_5]^-$, $Me_3SnW(CO)_4NO$, and $Me_3SnRe(CO)_5$.

Introduction

Series of nitrosyl carbonyls corresponding to $Ni(CO)_4$ [$Co(CO)_3NO$, $Fe(CO)_2(NO)_2$, etc.] and $Fe(CO)_5$ [$Mn(CO)_4NO$] are well known [2], and this isoelectronic principle has also been exemplified by the preparation of derivatives of the type $R_3SnFe(CO)_3NO$ [3], which are analogs of the well-known $R_3SnCo(CO)_4$ series [4]. The synthesis of the first members of a pseudo-pentacarbonylrhenium series, $XW(CO)_4NO$ (X = Cl, Br, I), was recently reported [5].

We wish to describe our preparation of an extensive series of compounds of the type $R_3M'M(CO)_4NO$ where M = Mo or W, and R_3M' is an organo-substituted Group IV element, for which the anions $[R_3M'M(CO)_5]^-$ [6] served as precursors.

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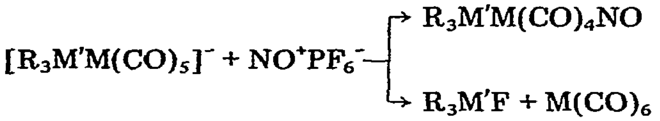
* For part XXIV, see ref. 1.

Results and discussion

The reaction of tetraethylammonium salts of the anions $[R_3M'M(CO)_5]^-$ [6] with nitrosonium hexafluorophosphate leads to the nitrosyl-substituted products, $R_3M'M(CO)_4NO$ (M = Mo, R_3M' = $GePh_3$, $SnPh_3$, $SnMe_3$, $PbPh_3$; M = W, R_3M' = $SiPh_3$, $SiPh_2Me$, $GePh_3$, $SnPh_3$, $SnMe_3$, $PbPh_3$). All reactions were performed in dichloromethane, often at —78°C, and yields varied from 7 to 54% depending upon M, M', and R. The tetracarbonylnitrosyl products formed pale yellow to red-orange crystals which are air stable, deteriorating only after long exposure. They are soluble in common organic solvents such as n-pentane, benzene, and dichloromethane, although solutions decompose after a few hours in the presence of air. When irradiated with ultraviolet light, an n-hexane solution of $Ph_3SiW(CO)_4NO$ completely decomposed to a non-carbonyl product within 8 h.

Another mode of reaction of NO^+ with neutral metal carbonyls [7] or carbonyl anions [8] involves oxidation rather than nitrosyl formation, and this may account for the variation in yield of the $R_3M'M(CO)_4NO$ compounds noted above. There appear to be two main reaction pathways:



$$[R_3M'M(CO)_5]^- + NO^+PF_6^- \rightarrow \begin{cases} R_3M'M(CO)_4NO \\ R_3M'F + M(CO)_6 \end{cases}$$

The fluoride derivatives (R_3M' = $SiPh_3$, $SiPh_2Me$, $GePh_3$, $SnPh_3$) were isolated and identified mass spectrometrically, and must arise by abstraction of fluoride ion from PF_6^-, the counter ion. Relatively large amounts of the hexacarbonyl were formed in all reactions, more so with molybdenum than with tungsten. Attempts to prepare the tetracarbonylnitrosyl compounds from $[Ph_3SiCr(CO)_5]^-$ and $[Ph_3GeCr(CO)_5]^-$ [6] were unsuccessful. It seems reasonable to suggest that the formation and yield of $R_3M'M(CO)_4NO$ products is determined by the stability of the M'—M bond to oxidation.

Cleavage of the bond between two metals by NO^+ has also been shown to occur for binuclear compounds such as $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ [9]. We have observed a related oxidative cleavage by NO^+ of $[Et_4N][MnW(CO)_{10}]$ [10] ($W(CO)_6$ and $[CH_3CNMn(CO)_5]^+$ were the only products identified) and of $[Et_4N]_2[W_2(CO)_{10}]$ [11] ($W(CO)_6$ was the main product, with some of the known $HW_2(CO)_9NO$ [12]).

Prior to the report by Barraclough, Bowden, Colton and Commons [5] on the reaction of $[XM(CO)_5]^-$ with NO^+ (M = Mo, W) we had studied the same reaction in the tungsten case and encountered difficulty in separating the desired products from $W(CO)_6$. Others have recently commented on the difficulty that this separation presents [13]. Accordingly, we mention here our finding that this separation problem can be circumvented by using excess $NO^+PF_6^-$ in acetonitrile as solvent; the hexacarbonyl is converted under these conditions to the known ionic acetonitrile complexes [8,9,14]. The reaction was monitored by IR, and $NO^+PF_6^-$ was added until the $W(CO)_6$ band was eliminated. Excess nitrosonium salt did not substantially decrease the yield of $XW(CO)_4NO$.

We have also observed that reaction of $[Et_4N][X_3SnW(CO)_5]$ (X = Cl, Br) with $NO^+PF_6^-$ proceeds with elision of SnX_2.

$$[X_3SnW(CO)_5]^- + NO^+ \xrightarrow{CH_2Cl_2} XW(CO)_4NO + SnCl_2 + CO$$

$(X = Cl, Br)$.

In fact, for X = Cl, a better yield of $ClW(CO)_4NO$ was obtained in this reaction than in the direct reaction with $[ClW(CO)_5]^-$.

Spectroscopic properties

The $R_3M'M(CO)_4NO$ complexes exist as the *trans* isomers, as shown by the IR spectra (Table 1). Two IR active carbonyl stretching frequencies (A_1 and E) are predicted for the C_{4v} *trans* isomer, and two are observed; the assignment follows from the relative intensities [15], with the very weak band near 2100 cm^{-1} assigned to the A_1 mode and the most intense carbonyl band near 2020 cm^{-1} as E. The A_1 vibration is scarcely visible at normal IR concentrations. A weak B_1 mode is observed in most cases since the actual symmetry is lower than C_{4v}. Bands due to the mono-^{13}CO substituted molecule (C_s symmetry) were also observed, although a concentrated solution was required for precise measurement of the A' (A_1) mode. A nitrosyl stretching band was observed around 1720 cm^{-1} at about half the intensity of the carbonyl E mode.

We have obtained the Raman spectrum of $BrW(CO)_4NO$ in the solid state and confirm the presence of two NO stretching frequencies (presumably due to crystal symmetry) reported previously [5]. A detailed IR and Raman study of this molecule has been carried out by Butler and Shaw [16].

Mass spectra were relatively simple, and the molecular ion was observed in all cases. Stepwise loss of CO groups from the molecular ion occurred; simultaneous loss of the NO group usually became prominent only after three CO groups had been lost, but in some cases was detected after loss of two CO groups

TABLE 1

CARBONYL AND NITROSYL STRETCHING FREQUENCIES, ASSIGNMENTS AND NMR DATA

Compound	Carbonyl stretching frequencies (cm^{-1})					Nitrosyl stretching frequencies (cm^{-1})
	all ^{12}CO (C_{4v})			mono-^{13}CO (C_s)		
	A_1	B_1	E	A' (A_1)	A' (E)	
$Ph_3GeMo(CO)_4NO$	2105	2046.5	2027.5	2097	1998	1722
$Ph_3SnMo(CO)_4NO$	2100.5	2040	2025	2092	1991	1725.5
$Me_3SnMo(CO)_4NO$[a]	2091		2013	2082	1979	1718.5
$Ph_3PbMo(CO)_4NO$	2103	2045.5	2030.5	2095	1997	1727
$W(CO)_4(NO)Cl$			2051		2017	1703
$W(CO)_4(NO)Br$	2136		2048.5		2016	1707
$W(CO)_4(NO)I$	2131.5		2046.5		2013.5	1711
$Ph_3SiW(CO)_4NO$	2102.5	2034.5	2015	2095	1985	1715.5
$Ph_2MeSiW(CO)_4NO$[b]	2098	2029.5	2009		1974	1713.5
$Ph_3GeW(CO)_4NO$	2104	2038	2019	2097	1985	1717.5
$Ph_3SnW(CO)_4NO$	2099.5	2034	2015	(2091)	1987.5	1720
$Me_3SnW(CO)_4NO$[c]	2089		2004.5	2082	1973	1715.5
$Ph_3PbW(CO)_4NO$	2100.5	2035.5	2020	2093	1986	1721

[a] τ (Sn—CH_3) = 9.8; J(Sn—CH_3) = 40 Hz; CCl_4 with TMS as external standard. [b] τ (Si—CH_3) = 9.15; CCl_4 with TMS as internal standard. [c] τ (Sn—CH_3) = 9.73; $J(^{117}Sn—CH_3)$ = 45.3 Hz, $J(^{119}Sn—CH_3)$ = 47.7 Hz; $CDCl_3$ with acetone (τ 7.95) as internal standard.

by small deviations in the observed isotope pattern. In the trimethyltin derivatives, mass spectra were more complex, showing loss of one or two methyl groups; ions of the following series were observed: $Me_3SnM(CO)_n(NO)^+$ (n = 4, 3); $Me_2SnM(CO)_n(NO)^+$ (n = 4, 3, 2, 1); $MeSnM(CO)_n(NO)^+$ (n = 3, 2, 1).

Comments on bonding

For comparison with other isoelectronic metal carbonyl series, it was of interest to calculate carbonyl stretching force constants for the *trans*-$R_3M'M(CO)_4NO$ derivatives. This has been done using the Cotton-Kraihanzel force field [17] and the parameters k_{CO}, k_{NO}, k_{CO-NO}' and k_i, (where k_i is the usual CO—CO interaction constant, with $k_{cis} = k_i$ and $k_{trans} = 2k_i$). The values obtained for a representative compound, $Ph_3GeW(CO)_4NO$, are: $k_{CO} = 16.77$, $k_{NO} = 13.49$, $k_{CO-NO} = 0.84$, $k_i = 0.16$ mdynes $Å^{-1}$.

A comparison of k_{CO} for $R_3M'W(CO)_4NO$ and $IW(CO)_4NO$ with $k_{equatorial}$ for the isoelectronic $R_3M'Re(CO)_5$ [18] and $IRe(CO)_5$ [19] showed differences of less than 0.2 mdyne $Å^{-1}$ between members of each isoelectronic pair.

A possible interpretation of the essentially similar equatorial force constants is as follows. The process of going from Re—CO to W—NO may be regarded as the transfer of a proton from the Re nucleus to the carbon nucleus. Two consequences of this process for π-bonding in the molecule can be envisaged. First, the lower nuclear charge resulting from the removal of a proton would destabilize the metal levels, increasing back-donation to the equatorial carbonyls, which would result in a lower k_{CO}. Alternatively, transfer of the proton to the axial ligand lower its π^* levels; hence back-donation to the axial ligand is increased, resulting in electron withdrawal from the metal and a stabilization of metal levels, which would bring about a higher k_{CO} for the equatorial carbonyls. Since the k_{CO} values are about the same, the two effects must roughly cancel. That is, the greater π electron acceptor capability of NO^+ compensates for the difference in nuclear potential. This discussion assumes that changes in the σ framework are minimal.

Further insight into the bonding in isoelectronic series is provided by the force constant and NMR coupling constant data on trimethyltin derivatives (Table 2).

It is evident from $k_{equatorial}$ that in the pentacarbonyltungsten anion, the lower nuclear potential relative to the pentacarbonylrhenium compound is not compensated, as it is in the nitrosyl. The electronic similarity of the $W(CO)_4NO$ and $Re(CO)_5$ moieties is further shown by the nearly identical proton—tin coupling constants. The usual arguments [20] relating *s*-character to coupling constants suggest that $[W(CO)_5]^-$ is a much less electronegative group than $W(CO)_4NO$ or $Re(CO)_5$, and this seems a reasonable conclusion.

TABLE 2

FORCE CONSTANTS AND NMR COUPLING CONSTANTS OF THE TRIMETHYLTIN DERIVATIVES

Compound	$k_{equatorial}$	$^2J(^{117}Sn—CH_3)$,	$(^{119}Sn—CH_3)$ (Hz)
$[Me_3SnW(CO)_5]^-$ [6]	15.06	35.5,	37.0
$Me_3SnW(CO)_4NO$	16.61	45.3,	47.7
$Me_3SnRe(CO)_5$ [18]	16.72	44.7,	46.7

TABLE 3

ANALYTICAL DATA, COLORS, YIELDS AND MELTING POINTS

Compound	Color	M.p. (°C)	Yield (%)	Found (%)				Calcd. (%)			
				C	H	N	Other	C	H	N	Other
$Ph_3GeMo(CO)_4NO$	orange	>70 (dec.)	33	48.45	2.91	2.50		48.76	2.79	2.58	
$Ph_3SnMo(CO)_4NO$	yellow-orange	112-114	12	45.43	2.71	2.45		45.93	2.57	2.38	
$Me_3SnMo(CO)_4NO$	orange	62-65	9	20.01	2.47	4.28		20.93	2.26	3.49	
$W(CO)_4(NO)Cl$	pale yellow	>90 (dec.)	14	13.38	0.0	4.09	Cl, 9.45	13.30	0.0	3.88	Cl, 9.81
$W(CO)_4(NO)Br$	pale yellow	>100 (dec.)	24	11.82	0.15	3.44	Br, 19.49 O, 19.34 W, 45.17	11.84	0.0	3.45	Br, 19.69 O, 19.34 W, 45.17
$W(CO)_4(NO)I$	pale yellow	>100 (dec.)	22	10.86	0.12	3.33	I, 28.88 O, 14.46 W, 42.38	10.61	0.0	3.09	I, 28.03 O, 17.67 W, 40.60
$Ph_3SiW(CO)_4NO$	orange	127	25	45.08	2.56	2.12		45.15	2.58	2.39	
$Ph_2MeSiW(CO)_4NO$	orange	69	10	39.21	2.75	2.63		39.02	2.50	2.68	
$Ph_3GeW(CO)_4NO$	yellow-orange	143-146	54	42.05	2.48	2.34	O, 12.59 W, 29.01 Ge, 11.49	41.96	2.40	2.22	O, 12.70 W, 29.19 Ge, 11.53
$Ph_3SnW(CO)_4NO$	orange	118-120	20	39.53	2.31	2.59		39.09	2.24	2.07	
$Me_3SnW(CO)_4NO$	yellow-orange	67	10	16.98	1.87	2.98		17.17	1.85	2.86	
$Ph_3PbW(CO)_4NO$	orange	>100 (dec.)	7	34.40	2.09	1.84	Pb, 27.39	34.57	1.98	1.83	Pb, 27.10

Experimental

Melting points were determined using a Kofler hotstage microscope. Analytical results (Table 3) were obtained by the Microanalytical Laboratory of this department and by the Alfred Bernhardt Microanalytisches Laboratorium, Elbach über Engelskirchen, West Germany.

Infrared spectra of the carbonyl and nitrosyl stretching regions were measured by means of a Perkin—Elmer Model 337 spectrometer at a scanning rate of 39 cm^{-1} min^{-1}, and recorded in expanded form (1 cm of chart $\approx$10 cm^{-1}) on an external recorder. Bands of gaseous CO (2147.08 cm^{-1}) and polystyrene (1583.1 cm^{-1}) were used to calibrate the spectra in the carbonyl and nitrosyl stretching regions respectively. Band positions listed in Table 1 were measured in n-hexane (Phillips Petroleum Co.) which was distilled from sodium wire under nitrogen before use. The relatively non-volatile solid samples were pumped at ca. 50°C under vacuum to remove traces of hexacarbonyl just prior to dissolution. Table 1 also lists as footnotes NMR data for the $MePh_2Si$ and Me_3Sn derivatives measured on a Varian A56/60 instrument.

Mass spectra of the nitrosyl derivatives were obtained using A.E.I. MS-12 and MS-9 instruments (70 eV, direct introduction of sample at lowest temperature necessary to produce the molecular ion).

Reactions were carried out using dichloromethane solvent, which was distilled from P_2O_5 prior to use. Reagent acetonitrile was used in some reactions; n-pentane and ether used in the extractions were also reagent grade.

The preparation of the Group IV—pentacarbonyl-metalates of molybdenum and tungsten was described previously [6]. The literature method [21] was used to prepare $[Et_4N][XW(CO)_5]$ (X = Cl, Br, I). Nitrosonium hexafluorophosphate was purchased from the Ozark-Mahoning Co. and was used without further purification.

Preparation of $Ph_3GeMo(CO)_4NO$

A Schlenk tube containing a mixture of $[Et_4N][Ph_3GeMo(CO)_5]$ (1.5 g, 2.2 mmol) and $NOPF_6$ (0.5 g, 2.8 mmol) was evacuated and ca. 30 ml of dichloromethane was distilled into the vessel at —78°C. After the reaction mixture was warmed to —10°C (salt/ice bath) and stirred for 2.5 h, the solution had turned red-brown. The solvent was removed under reduced pressure and the residue was extracted with five 50-ml portions of n-pentane or until the extracts were colorless. The solvent was removed using water aspiration. A water cooled probe was fitted to the flask and $W(CO)_6$ and Ph_3GeF, formed as by-products in the reaction, were sublimed in high vacuum at 25-40°C over a period of 2-3 days. The sublimation residue was then recrystallized from n-pentane affording orange crystals of the analytical sample (0.4 g, 33% yield).

The $Ph_3SnMo(CO)_4$, $Ph_3GeW(CO)_4NO$, and $Ph_3SnW(CO)_4NO$ complexes were prepared in an analogous manner.

Preparation of $IW(CO)_4NO$

To a solution of $[Et_4N]$ $[IW(CO)_5]$ (2.0 g, 3.4 mmol) in 10 ml acetonitrile was added dropwise a solution of $NOPF_6$ (ca. 2 *M*) in the same solvent. The addition was continued until the IR bands due to $W(CO)_6$ had diminished considerably. The solvent was removed in vacuo and the product extracted with a total of 300 ml n-pentane. The yellow solution was filtered and concentrated to ca. 50 ml. On cooling at —78°C yellow crystals formed; these were filtered and sublimed at room temperature to give 0.35 g (22% yield) of the product.

The $BrW(CO)_4NO$ complex was prepared in an analogous fashion with the exception that the product was extracted with 1/1 dichloromethane/ether solution.

Preparation of $ClW(CO)_4NO$

To a solution of $[Et_4N][Cl_3SnW(CO)_5]$ (1.4 g, 2.1 mmol) in dichloromethane (40 ml) solid $NOPF_6$ (0.5 g, 2.8 mmol) was added slowly at room temperature and the solution stirred for 15 min. After removing the solvent in vacuo, the residue was extracted with 300 ml n-pentane, and after filtering, the solvent was removed on a rotary evaporator. The solid was transferred to a sublimer and $W(CO)_6$ was sublimed at room temperature and 0.25 torr. After removal of the $W(CO)_6$ from the sublimation probe, the product was sublimed at 60°C and 0.1 g (14% yield) of pale yellow crystals were obtained.

Preparation of $Ph_3SiW(CO)_4NO$

To a solution of $[Et_4N][Ph_3SiW(CO)_5]$ (3.0 g, 4.2 mmol) in 50 ml of dichloromethane, 0.5 g of $NOPF_6$ was added and the solution stirred at room temperature. The progress of the reaction was followed by the disappearance of starting material bands in the IR spectrum. An additional 0.5 g of $NOPF_6$ was added after 0.5 h and stirring continued for 1.5 h. Ether (20 ml) was added, the solution was filtered and the solvents were removed in vacuo. The residue was extracted with four 50-ml portions of n-pentane solution concentrated to ca. 50 ml. On cooling to 0°C crystals formed, and these were transferred to a sublimer. The Ph_3SiF and $W(CO)_6$ formed in the reaction were sublimed at 0.05 torr. The orange solid left behind was recrystallized from n-pentane affording 0.6 g (25% yield) of product.

Preparation of $MePh_2SiW(CO)_4NO$

Dichloromethane was vacuum distilled into a Schlenk tube containing $[Et_4N][MePh_2SiW(CO)_5]$ (2.5 g, 3.8 mmol) and $NOPF_6$ (0.7 g, 4.0 mmol). The solution was stirred at —78°C for 7 h under closed vacuum and then warmed to room temperature before removal of the solvent. The residue was extracted with 150 ml n-pentane, filtered and the solvent removed leaving behind a red oil. An orange oily solid, which was identified as mainly $MePh_2SiF$, sublimed onto a Dry Ice/acetone probe under vacuum. The residue was pumped for 2 days at room temperature to remove $W(CO)_6$ and residual $MePh_2SiF$. Crystallization of the solid from n-pentane afforded orange crystals of $MePh_2SiW(CO)_4NO$ (0.4 g, 20% yield).

The preparation of the complexes $MePh_2SiMo(CO)_4NO$ and $Ph_3SiMo(CO)_4NO$ was attempted in a similar manner but only $Mo(CO)_6$ was isolated.

Preparation of $Me_3SnW(CO)_4NO$

Dichloromethane (30 ml) was distilled into a reaction vessel containing $[Et_4N][Me_3SnW(CO)_5]$ (2.0 g, 3.2 mmol) and $NOPF_6$ (0.7 g, 4.0 mmol) cooled to —78°C. The mixture was kept at this temperature for three days. The solvent was removed by vacuum distillation into a trap cooled to —196°C. The residue was extracted with several portions of n-pentane, filtered and the solvent removed by water aspiration vacuum. The residue was charged into a sublimer and the volatile $Me_3SnW(CO)_4NO$ was sublimed onto a water-cooled probe together with some $W(CO)_6$. The product was washed off the probe by squirting with ca. 10 ml of n-hexane, leaving most of the $W(CO)_6$ behind. This was then chromatographed on a Florisil column eluting as a red band with n-hexane. Cooling at —20°C overnight afforded orange crystals of $M_3SnW(CO)_4NO$ (0.16 g, 10% yield). The unsublimed material left behind was not identified but showed both carbonyl and nitrosyl bands in the infrared spectrum.

The $Me_3SnMo(CO)_4NO$ complex was prepared using similar conditions.

Preparation of $Ph_3PbW(CO)_4NO$

A dichloromethane solution of $[Et_4N][Ph_3PbW(CO)_5]$ (4.0 g, 4.5 mmol) and $NOPF_6$ (1.0 g, 5.7 mmol) was stirred at —78°C for 9 h. The solvent was removed under reduced pressure with the temperature of the reaction vessel maintained at —78°C. The residue was extracted with 6 × 30-ml portions of n-pentane, filtered and the solvent removed. The large amounts of $W(CO)_6$ and other byproducts formed in the reaction were sublimed. Red crystals of product were obtained by crystallization of the unsublimed material from n-pentane (0.2 g, 7% yield).

The $Ph_3PbMo(CO)_4NO$ complex was prepared under similar conditions. Because of low yield a sufficient sample for analysis was not obtained and the compound was characterized only mass spectrometrically.

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