Interaction of Nitric Oxide with Paramagnetic and Diamagnetic Alkyls of Titanium, Zirconium, Vanadium, Niobium, and Tantalum

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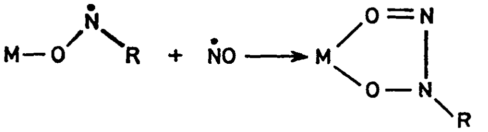
An earlier observation that there is a profound difference in the way paramagnetic and diamagnetic alkyl compounds of transition metals react with nitric oxide is extended. The reaction of NO with bis(η^5-cyclopentadienyl)-dimethylniobium(IV), d^1, can be followed by nuclear magnetic resonance spectra and intermediates detected. The final product of the reaction is bis(η^5-cyclopentadienyl)methyloxoniobium(V), which with excess of NO, gives the *N*-methyl-*N*-nitrosohydroxylaminato-complex $Nb(\eta\text{-}C_5H_5)_2(O)[ON(Me)NO]$. An intermediate niobio-aziridine collapses with methylnitrene transfer to give azomethane, and in the presence of styrene, an aziridine. Tetrakis(trimethylsilylmethyl)vanadium(IV) gives with NO the previously known $VO(CH_2SiMe_3)_3$ while the titanium(III), d^1, compounds $Ti(\eta\text{-}C_5H_5)_2R$ (R = Ph or CH_2Ph) lose both cyclopentadienyl and aryl or benzyl groups to give a trimeric species $Ti_3(\eta\text{-}C_5H_5)_3O_4(NO)$ that has oxo-bridges and a bent Ti–NO group. The diamagnetic alkyls of titanium and zirconium, TiR_4, TiR_3Cl, TiR_2Cl_2, ZrR_4, and ZrR_2Cl_2 (R = CH_2SiMe_3 or CH_2CMe_3) and NO give *N*-alkyl-*N*-nitrosohydroxylaminato-complexes. The titanium compounds are six-co-ordinate with unidentate and bidentate ON(R)NO groups, while the zirconium compounds are eight-co-ordinate with chelate groups only. The pentamethyls MMe_5 (M = Nb or Ta) and NO give $NbMe_2[ON(Me)NO]_3$ and $\{TaMe_3[ON(Me)NO]_2\}_2$ respectively.

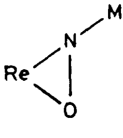
THE reaction of nitric oxide with transition-metal alkyls or complex alkyls leads to the formation of *N*-alkyl-*N*-nitrosohydroxylaminato-compounds [1,2] by the fast reaction of NO with the radical intermediate first formed by alkyl transfer [2] [see equations (i) and (ii)].


(i)


(ii)

The structures of tungsten,[2] rhenium,[3] and tantalum [4] chelate complexes have been determined by *X*-ray diffraction study and the chelate nature of the ON(R)NO group confirmed.

By contrast, the paramagnetic methyl, $ReOMe_4$, which has a single unpaired electron, was found to react with NO to give *cis*-trimethyldioxorhenium(VII) and azomethane, $CH_3N{=}NCH_3$. It was suggested [5] that the unstable intermediate first formed is diamagnetic and that this has a structure with either a three-membered ring (1) or a bridge (2a) [a bridge of type (2b) was considered less likely since the normal co-ordination number of rhenium(VII) would be exceeded], either of which can decompose with loss of methylnitrene, leading to $CH_3N{=}NCH_3$ and formation of a Re=O bond. This reaction thus results in deoxygenation of nitric oxide.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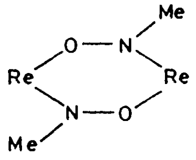
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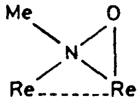

(2b)

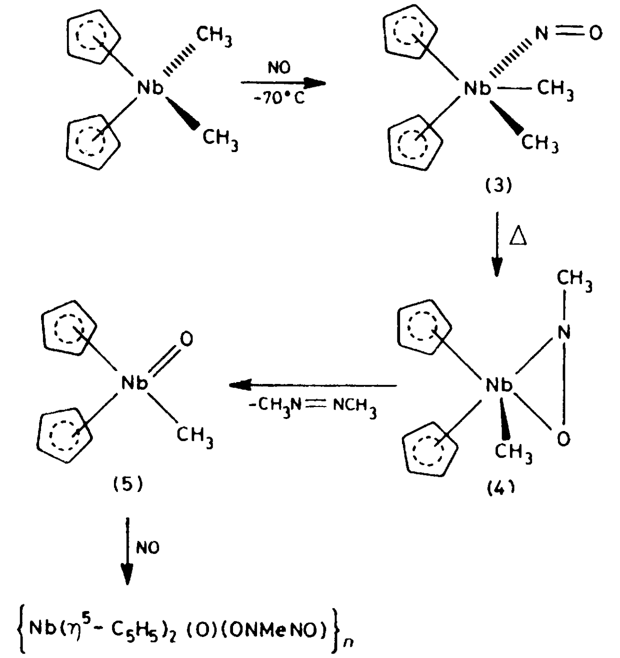
Paramagnetic alkyls with two unpaired electrons such as $Cr(CH_2SiMe_3)_4$ also reacted with nitric oxide [6] but the products were complex and not characterised.

η^2-Nitrosoalkane or metallo-oxoaziridine complexes of type (1) have recently been made from substituted hydroxylamines [7,8] and the structure of a molybdenum complex with a η^2-ONH group has also been characterised,[9a] while a related η^2-ON(H)(CH_3) compound has been structurally characterised by *X*-ray methods.[9b] A cobalt compound $[CoMe(\mu\text{-}MeNO)(PMe_3)_2]$ has been obtained from $CoMe_2(PMe_3)_3$ [10] and a bridge of type (2b) was proposed.

RESULTS AND DISCUSSION

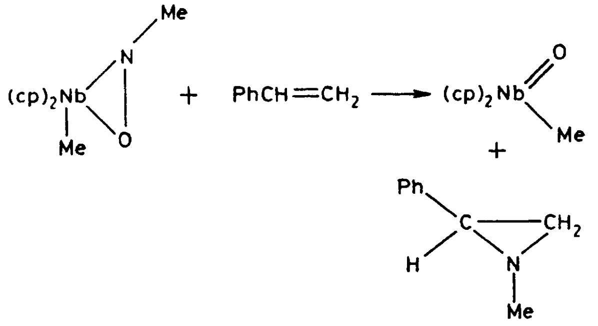
Interaction of Nitric Oxide with Paramagnetic Alkyls.—The red d^1 compound $Nb(\eta^5\text{-}C_5H_5)_2Me_2$ [11] reacts rapidly with an excess of nitric oxide at room temperature in light petroleum to give a very insoluble white precipitate of stoicheiometry $Nb(cp)_2(O)[ON(Me)NO]$ (cp = cyclopentadienyl) which is diamagnetic and has a band in the i.r. at 865 cm^{-1} that can be ascribed to Nb=O as well as bands typical for the *N*-methylnitrosohydroxylaminato-group.[2] It may well be polymeric as is a zirconium compound,[1a] with bridging ON(Me)NO groups. At −70 °C, however, a pale yellow toluene-soluble precipitate is obtained. This is diamagnetic, and has a band at 1 670 cm^{-1} that can be assigned to a bent Nb(NO) group.[12] The ^{1}H n.m.r. spectrum has two peaks due to non-equivalent methyl groups and one due to η^5-C_5H_5. The reaction sequence shown in the Scheme is proposed, where (3) and (4) could be characterised only spectroscopically.

On monitoring the n.m.r. spectrum at room temperature, the δ 0.12 p.p.m. (Nb–CH_3) peak diminishes and is replaced by one at 2.83 p.p.m. (N–CH_3), consistent with methyl migration to form an unstable η^2-nitrosomethane complex (4), which then decomposes with elimination of $CH_3N{=}NCH_3$. The latter was identified by its mass peak at 58 and characteristic fragmentation pattern.[13] The resulting oxo-methyl complex, (5), is readily isolated and characterised. Additional NO converts it to the insoluble white compound noted above.



SCHEME

Although we cannot be certain that (4) has a three-membered oxo-aziridine ring and not a bridge of type (2), the confirmation of the three-membered ring in one case[7] suggests that a η^2-nitrosomethane structure is most likely. Additional evidence for nitrene transfer, however, is the reaction of (4), made *in situ*, with styrene to give an aziridine.



This transfer is similar to that found for molybdenum η^2-PhNO compounds[7,8] except that in the latter the aziridine was not isolated and the work-up led to allylic amines. When the reaction mixture from styrene or 1-methylcyclohexene with the niobium compound was worked up in acidic conditions, polymeric amines (*cf.* ref. 14) were also obtained.

The reaction of the d^1 alkyl $V(CH_2SiMe_3)_4$ with NO initially gives a red solution which is unstable and on warming deposits yellow needles of $VO(CH_2SiMe_3)_3$, but in this case, no further reaction to give a *N*-alkyl-*N*-nitrosohydroxylaminato-complex occurs, presumably because of co-ordinative saturation of vanadium(V) in this oxo-alkyl.

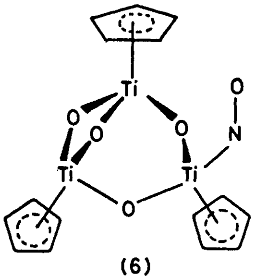
The paramagnetic d^1 titanium compounds $Ti(\eta^5-C_5H_5)_2R$ ($R = C_6H_5$ or $CH_2C_6H_5$) react in both cases to give the same product. The sparingly soluble complex has the stoicheiometry $Ti_3(cp)_3O_4(NO)$, where not only has the phenyl or benzyl group been lost, but also one C_5H_5 group per titanium. This difference from the vanadium and niobium compounds can be ascribed to the well known preference of titanium to form Ti–O–Ti, rather than Ti=O bonds.[12] The initial transfer of Ph or $PhCH_2$ to NO can be expected to give an unstable '$(cp)_2Ti=O$' intermediate which then reacts further in presence of nitric oxide. Loss of a C_5H_5 ring and formation of Ti–O–Ti bridges has also been observed in the formation of the complex $Ti_6(cp)_6O_8$ in the reaction of $Ti(cp)_2(CO)_2$ with carbon monoxide and hydrogen and in which a η^2-OCH intermediate was invoked.[15] If we propose that there is an intermediate $Ti_3(C_5H_5)_3O_4$, which would have one unpaired electron, this could either dimerise to $Ti_6(cp)_6O_8$ or, in the presence of NO, could be trapped by reaction with NO to give $Ti_3(cp)_3O_4(NO)$. For this complex we propose the structure (6), where the $Ti(\eta^5-C_5H_5)$ units are linked by oxo-bridges, on the basis of spectroscopic data. Thus, the ^1H n.m.r. spectrum has two peaks (δ 6.30 and 6.37 p.p.m.) in the ratio 2 : 1 due to the two environments of the C_5H_5 rings, while the i.r. band at 1 550 cm^{-1} can be assigned to a bent Ti(NO) group.

Interaction of Nitric Oxide with Diamagnetic Alkyls.—The interaction of NO with several titanium and zirconium alkyls follows the same route as found previously[1,2] and leads to *N*-alkyl-*N*-nitrosohydroxylaminates.

The zirconium alkyls give the compounds $Zr[ON(R)NO]_4$ ($R = CH_2SiMe_3$ or CH_2CMe_3) that are monomeric and stable in dry air, though hygroscopic; they are evidently eight-co-ordinate as in (7). The partially alkylated compounds, MR_2Cl_2 (M = Ti or Zr; $R = CH_2SiMe_3$ or CH_2CMe_3) (which have been made *in situ* by exchange reactions but not isolated), absorb four equivalents of NO and give octahedral complexes $MCl_2[ON(R)NO]_2$ whose i.r. bands indicate *cis*-M–Cl groups as in (8). However, $Ti(CH_2SiMe_3)_4$ gives a monomeric, more highly coloured low-melting solid $Ti[ON(R)NO]_4$ whose ^1H n.m.r. spectrum indicates two types of alkyl group bound to nitrogen so that there must be both unidentate and chelate groups as in (9). An i.r. band at *ca.* 1 550 cm^{-1} can be ascribed to ν(NO) of the unidentate group. Although a unidentate group was proposed for $Zr(\eta^5-C_5H_5)_2(CH_3)[ON(CH_3)NO]$[1a] this compound does not have a band in the 1 550 cm^{-1} region and the ON(Me)NO group is probably chelated as suggested previously.[2] The alkyl $TiCl(CH_2CMe_3)_3$ also gives a compound, probably of structure (10), that has a band at 1 550 cm^{-1} and two types of neopentyl groups bound to nitrogen.

The pentamethyls of niobium and tantalum, like

WMe_6,[2] react by successive stages with NO until the maximum or preferred co-ordination number is reached. Niobium gives $NbMe_2[ON(Me)NO]_3$ which is monomeric with equivalent chelate ligands and two methyl groups remaining bound to Nb as in (11). The rather similar $NbCl_2Me[ON(Me)NO]_2$, obtained from $NbCl_2Me_3$, is only seven-co-ordinate[4] however, and this difference is presumably due to the greater steric bulk of the halogen atoms (*cf.* ref. 1*b*).



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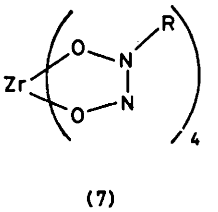

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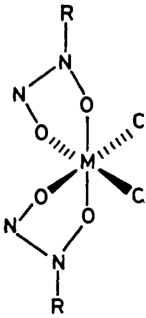

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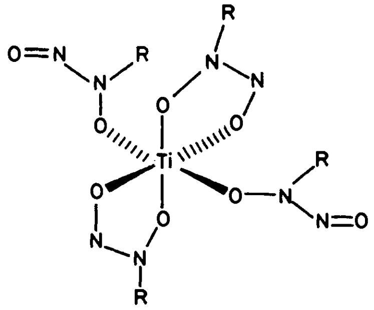

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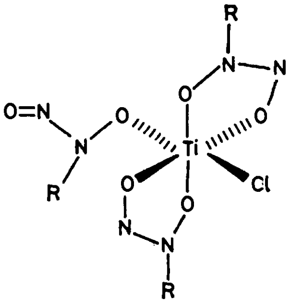

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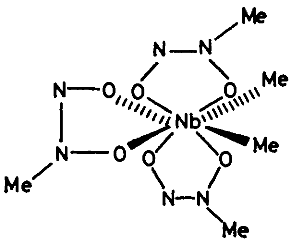

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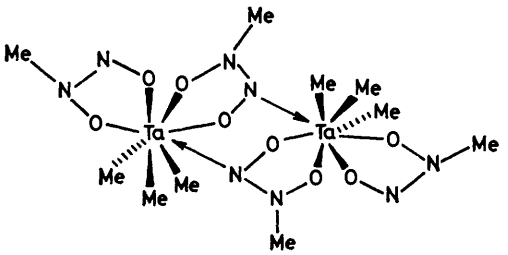

(12)

Pentamethyltantalum gives a white dimeric complex, $\{TaMe_3[ON(Me)NO]_2\}_2$; there is no band at *ca.* 1 550 cm^{-1} and the ^1H n.m.r. spectrum indicates two types of *N*-methyl-*N*-nitrosohydroxylaminato-groups as well as three equivalent methyl groups bound to tantalum. The structure (12) is suggested.

EXPERIMENTAL

All operations were carried out under nitrogen or *in vacuo*. Nitric oxide was from British Oxygen Co. The diethyl ether, tetrahydrofuran, toluene, and light petroleum (b.p. 40—60 °C) were dried over sodium and distilled under nitrogen. Melting points were determined in sealed capillaries; molecular weights were determined cryoscopically in benzene or osmometrically in dichloromethane, using a Perkin-Elmer–Hitachi osmometer.

Hydrogen-1 n.m.r. spectra were measured on Perkin-Elmer R12A or R32 instruments in C_6D_6, C_8D_8, or $CDCl_3$, i.r. spectra in Nujol mulls on a Perkin-Elmer 457 instrument. Mass spectra were determined on a VG Micromass spectrometer.

Microanalyses were by the Pascher, Bonn, and Imperial College laboratories. Note that analytical data (Table) on *N*-nitrosohydroxylaminato-compounds are often unsatisfactory[2] due to difficulties with combustion. The yields are *ca.* 95%, unless otherwise stated.

Interaction of Nitric Oxide and Bis(η^5-*cyclopentadienyl*)-*dimethylniobium*(IV).— *Bis*(η^5-*cyclopentadienyl*)*dimethyl*(*nitrosyl*)*niobium*, *bis*(η^5-*cyclopentadienyl*)*methyl*(*oxo*)-*niobium*(V), *and bis*(η^5-*cyclopentadienyl*)-N-*methyl*-N-*nitrosohydroxylaminato-oxoniobium*(V). Nitric oxide was slowly passed into a solution of $Nb(cp)_2Me_2$[11] in light petroleum at −70 °C until the red colour of the solution disappeared. The yellow precipitate of the adduct $Nb(cp)_2Me_2(NO)$ was collected at −70 °C, washed with cold light petroleum, and freed from solvent by pumping at −20 °C (10^{-3} mmHg).* Although the compound was too unstable to analyse properly, it may be handled in nitrogen briefly and i.r. and n.m.r. spectra measured. I.r.: 1 670 cm^{-1} (N=O); ^1H n.m.r.: δ 0.12s (CH_3), 0.94s (CH_3), and 5.92 ($2 \times C_5H_5$).

When the same reaction was carried out in toluene, the complex remained in solution. When this solution, or a solution of the isolated complex in deuteriotoluene, was allowed to warm in a n.m.r. tube, the changes in the methyl resonances could be followed readily at room temperature.

The nitric oxide adduct or its solutions were readily converted to $Nb(cp)_2O(CH_3)$ and for direct synthesis of the latter, the light petroleum precipitate above was warmed to 25 °C, dissolved in warm toluene, and the solution cooled to −30 °C to give the crystalline compound which was collected, washed with diethyl ether, and dried (*ca.* 80%). I.r.: 835 cm^{-1} (Nb=O); ^1H n.m.r.: δ 0.88s (CH_3) and 5.94s ($2 \times C_5H_5$).

Interaction of NO and $Nb(cp)_2Me_2$ in toluene at 25 °C gave a white precipitate of $Nb(cp)_2(O)[ON(Me)NO]$ which was collected, washed with light petroleum and tetrahydrofuran, and dried *in vacuo*. It was too insoluble to determine either the n.m.r. spectra or molecular weight and consequently, it may be polymeric with bridging ON(Me)NO groups. I.r.: 1 190 cm^{-1}, 1 255 cm^{-1} (ONNO), and 865 cm^{-1} (Nb=O).

Interaction of Styrene with η^2-*Nitrosomethane Intermediate*.—A solution of $Nb(cp)_2Me_2(NO)$, from $Nb(cp)_2Me_2$ (*ca.* 2 g) in toluene (40 cm^3) at −70 °C, containing an excess (*ca.* 2 cm^3) of freshly distilled styrene was allowed to warm

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* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

to 25 °C and was stirred for several hours. The solution was reduced to *ca.* 5 cm^3, transferred to a silica column, and eluted with toluene–light petroleum, which removed styrene, and then with dichloromethane. The collected solvent was removed and 1-methyl-2-phenylaziridine [16] was distilled at 35 °C (0.3 mmHg). It was characterised by its mass spectrum 133 (calc. 133) and ^{1}H n.m.r. spectrum δ 1.5m, 1.7m, 2.1m (3 × C–H), 2.38s (1 × CH_3), and 7.2m (5 × Ph–H).

Interaction of Nitric Oxide with Tetrakis(*trimethylsilylmethyl*)*vanadium*(IV).—Through a solution of $V(CH_2SiMe_3)_4$ [6] in light petroleum at −70 °C, was passed NO until the green solution became red. On warming to room temperature, the solution became yellow and deposited yellow needles of $VO(CH_2SiMe_3)_3$,[6] essentially quantitatively; although $(Me_3SiCH_2)_2N_2$ is presumably formed, we have not isolated this material.

Analytical data of new compounds

Compound	Colour	Decomp. (θ_c/°C)	Analysis (%) [a] C	H	N	*M* [a]
$Ti[ON(CH_2SiMe_3)NO]_4$	Orange	40	29.7 (30.2)	6.8 (6.9)	17.6 (17.6)	605 [b] (636)
$TiCl_2[ON(CH_2SiMe_3)NO]_2$	White	130	22.3 (23.2)	4.6 (5.3)	12.7 (13.6)	
$TiCl[ON(CH_2CMe_3)]_3$	Yellow	60	38.0 (37.8)	6.8 (6.9)	16.8 (17.6)	455 [b] (476)
$TiCl_2[ON(CH_2CMe_3)NO]_2$	White	130	30.6 (31.5)	6.8 (5.8)	12.8 (14.7)	381 [c] (381)
$Ti_3(cp)_3O_4(NO)$	Orange	180	46.0 (43.6)	4.1 (3.6)	4.0 [d] (3.4)	420 [b] (413)
$Zr[ONCH_2SiMe_3NO]_4$	White	120	28.5 (28.3)	6.1 (6.5)	16.1 (16.5)	765 [b] (679)
$ZrCl_2[ON(CH_2SiMe_3)NO]_2$	White	140	20.5 (21.1)	4.6 (4.8)	12.2 (12.3)	
$Zr[ON(CH_2CMe_3)NO]_4$	White	180	39.0 (39.0)	7.2 (7.2)	18.0 (18.2)	580 [b] (615)
$Nb(cp)_2(O)Me$	White	140	51.0 (52.0)	5.1 (5.1)	0 (0)	270 [b] (254)
$Nb(cp)_2(O)[ON(Me)NO]$	White	160	41.2 (41.7)	3.6 (4.1)	8.9 (8.9)	
$NbMe_2[ON(Me)NO]_3$	Yellow	150	17.1 (17.2)	3.9 (4.3)	22.1 (24.1)	380 [e] (348)
$\{TaMe_3[ON(Me)NO]_3\}_2$	White	70	15.0 (15.9)	3.3 (5.0)	13.0 (15.0)	700 [e] (750)

[a] Calculated values are given in parentheses. [b] Osmometrically. [c] Mass spectrum. [d] Direct oxygen analysis 18.9 (19.4). [e] Cryoscopically.

Interaction of Nitric Oxide with Bis(η^5-*cyclopentadienyl*)-*phenyl- and -benzyl-titanium*(III).—The compounds [17] in diethyl ether reacted with NO to form an orange precipitate which was collected, washed with diethyl ether, and recrystallised from dichloromethane. The product in both cases is $Ti_3(\eta^5\text{-}C_5H_5)_3O_4(NO)$. I.r.: 1 550 cm^{-1} (NO); ^{2}H n.m.r.: δ 6.30s (2 × C_5H_5) and 6.37s (C_5H_5).

Tetrakis(N-*nitroso*-N-*trimethylsilylmethylhydroxylaminato*)*titanium*(IV).—In light petroleum at 0 °C, $Ti(CH_2SiMe_3)_4$ [18] reacted with NO to give a yellow-orange solution. Removal of solvent and crystallisation from diethyl ether gave an orange solid. I.r.: 1 550 cm^{-1} (NO); ^{1}H n.m.r.: δ 0.06, 0.14s (CH_3), 3.47, and 3.76s (CH_2).

Dichlorobis(N-*nitroso*-N-*trimethylsilylmethylhydroxylaminato*)*titanium*(IV).—In light petroleum NO and $TiCl_2(CH_2SiMe_3)_2$ [made *in situ* by interacting $TiCl_4$ and $Ti(CH_2SiMe_3)_4$ in diethyl ether] reacted to give a white precipitate which was recrystallised from toluene–tetrahydrofuran (1 : 1). I.r.: 320 and 350 cm^{-1} (Ti–Cl); ^{1}H n.m.r.: δ 0.90s (CH_3) and 3.27s (CH_2).

Chlorotris(N-*neopentyl*-N-*nitrosohydroxylaminato*)-*titanium*(IV).—As above, but from $TiCl(CH_2CMe_3)_3$ [made *in situ* by interacting $TiCl_4$ and $Ti(CH_2CMe_3)_4$ in diethyl ether] to give a yellow crystalline solid from diethyl ether. I.r.: 1 545 (NO) and 345 (Ti–Cl) cm^{-1}; ^{1}H n.m.r.: δ 1.02s (CH_3), 1.12s (2 × CH_3), 3.58s (2 × CH_2), and 3.72s (CH_2).

Dichlorobis(N-*neopentyl*-N-*nitrosohydroxylaminato*)-*titanium*(IV).—As above but from $TiCl_2(CH_2CMe_3)_2$ [*in situ* from $TiCl_4$ and $Ti(CH_2CMe_3)_4$ in diethyl ether] to give a white crystalline solid from toluene–tetrahydrofuran (1 : 1). I.r.: 320 and 355 cm^{-1} (Ti–Cl); ^{1}H n.m.r.: δ 0.88s (CH_3) and 350s (CH_2).

Tetrakis(N-*nitroso*-N-*trimethylsilylmethylhydroxylaminato*)*zirconium*(IV).—From $Zr(CH_2SiMe_3)_4$ [18] in light petroleum a white solid recrystallised from toluene. ^{1}H n.m.r.: δ 0.11s (CH_3) and 3.52s (CH_2).

Dichlorobis(N-*nitroso*-N-*trimethylsilylmethylhydroxylaminato*)*zirconium*(IV).—From $ZrCl_2(CH_2SiMe_3)_2$ [made *in situ* by stoicheiometric interaction of $ZrCl_4$ and $Zr(CH_2SiMe_3)_4$] in light petroleum recrystallised from toluene–tetrahydrofuran (1 : 1). I.r.: 330 and 350 cm^{-1} (Zr–Cl); ^{1}H n.m.r.: δ 0.04s (CH_3) and 3.24s (CH_2).

Tetrakis(N-*neopentyl*-N-*nitrosohydroxylaminato*)*zirconium*(IV).—From $Zr(CH_2CMe_3)_4$ [18] in light petroleum a white precipitate crystallised from toluene. ^{1}H n.m.r.: δ 0.98 (CH_3) and 3.55s (CH_2).

Dimethyltris(N-*methyl*-N-*nitrosohydroxylaminato*)*niobium*(V).—Interaction of NO and $NbMe_5$ [19] in light petroleum at −70 °C gave a yellow precipitate which was collected, extracted with toluene at 25 °C, and the solution cooled to −30 °C to give orange-yellow crystals. ^{1}H n.m.r.: δ 0.63s (Nb–CH_3) and 3.2s (N–CH_3).

Trimethylbis(N-*methyl*-N-*hydroxylaminato*)*tantalum*(V).—As above, but using $TaMe_5$ [19] to give colourless crystals. ^{1}H n.m.r.: δ 1.78s (Ta–CH_3), 3.24s, and 4.18s (N–CH_3).

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