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REACTIONS OF METHYLNIOBIUM(V) AND METHYLTANTALUM(V) CHLORIDES WITH CARBODIIMIDES

JOHN D. WILKINS*
Donnan Laboratories, University of Liverpool, Liverpool L69 3EX (Great Britain)
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Summary

The chlorides Me_xMCl_{5-x}, M = Nb, Ta, x = 1, 2, 3 react with carbodiimides RNCNR (R = isopropyl, cyclohexyl, *p*-tolyl) to give products of the types $MCl_4[NR—C(Me)=NR]$, $MeMCl_3[NR—C(Me)=NR]$, $MCl_3[NR—C(Me)=NR]_2$, $Me_2MCl_2[NR—C(Me)=NR]$, $MeMCl_2[NR—C(Me)=NR]_2$, which contain bidentate acetamidine groups arising from insertion of the carbodiimide into the metal—carbon bond. The products have been characterised by elemental analysis IR and proton NMR spectra.

Introduction

As part of a study of the reactions of methylniobium(V) and methyltantalum(V) chlorides their reactions with carbodiimides have been investigated [1–3]. Reactions of carbodiimides with early transition metal alkyls have not been previously investigated but their reactions with Grignard reagents [4] and other main group organometallic compounds have been reported [5]. Carbodiimides also insert into Ti—N and Zr—N bonds [6].

Results and discussion

The reactions of the alkyls Me_xMCl_{5-x} (M = Nb, Ta, x = 1–3) with the carbodiimides (RNCNR) R = isopropyl (PRCD), tert-butyl (BUCD), cyclohexyl (CCD) and *p*-tolyl (PTCD) have been investigated. Products containing disubstituted acetamidine groups have been characterised in most cases. The carbodiimide inserts into the M—C bonds in a manner analogous to that reported for the related reactions with RNCO and RNCS [1, 2]. The complexes prepared together with appropriate analytical data are listed in Table 1.

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* Present address, Department of Chemistry, University College London, 20 Gordon St., London WC1H OAJ.

TABLE 1

COMPLEXES PREPARED AND ANALYTICAL DATA

Complex [a]	Colour	Analysis found (calcd.) (%)	
		Cl	M
$NbCl_4$[PR]	Red	37.3 (37.7)	24.2 (24.7)
$NbCl_4$[CY]	Violet	30.4 (31.1)	20.5 (20.4)
$NbCl_4$[PT]	Dark red-brown	30.0 (30.0)	20.0 (19.7)
$TaCl_4$[PR]	Orange-red	30.2 (30.6)	38.7 (39.0)
$TaCl_4$[CY]	Bright red	26.0 (26.1)	33.3 (33.3)
$TaCl_4$[PT]	Orange-red	25.5 (25.3)	32.2 (32.3)
$MeNbCl_3$[PR]	Brown-red	29.7 (29.9)	25.7 (26.1)
$MeNbCl_3$[CY]	Red-brown	24.2 (24.4)	21.7 (21.3)
$MeNbCl_3$[PT]	Orange-brown	23.8 (23.5)	20.6 (20.5)
$MeTaCl_3$[PR]	Orange-red	23.6 (24.0)	40.7 (40.8)
$TaCl_3[PT]_2$	Red	18.7 (18.7)	32.0 (31.8)
$MeTaCl_3$[CY]	Orange-red	20.0 (20.3)	34.2 (34.6)
$MeTaCl_3$[PT]	Yellow-orange	19.4 (19.7)	33.4 (33.5)
Me_2NbCl_2[PR]	Red-brown	20.5 (21.2)	27.4 (27.7)
Me_2NbCl_2[CY]	Red	16.8 (17.1)	22.6 (22.4)
$MeNbCl_2[CY]_2$	Red	11.6 (11.4)	14.7 (15.0)
Me_2TaCl_2[PR]	Yellow	17.0 (16.8)	43.1 (42.8)
$MeTaCl_2[PR]_2$	Yellow-orange	12.8 (12.9)	33.1 (32.9)
Me_2TaCl_2[CY]	Yellow	14.1 (15.8)	36.1 (35.3)
$MeTaCl_2[CY]_2$	Yellow-orange	9.8 (9.9)	24.8 (25.1)
Me_2TaCl_2[PT]	Yellow	13.9 (13.7)	33.6 (34.9)
$MeTaCl_2[PT]_2$	Yellow	9.7 (9.6)	24.8 (24.4)

[a] [PR] = [N-i-Pr—C(Me)=N-i-Pr], [CY] = [N(C_6H_{11})—C(Me)=NC_6H_{11}], C_6H_{11} = cyclohexyl, [PT] = [N(p tolyl)—C(Me)=N(p tolyl)].

(a). Reactions with $MeMCl_4$

Solutions of $MeNbCl_4$ react rapidly with PRCD, CCD and PTCD at room temperature yielding products of the type MCl_4[NR—C(Me)=NR] containing the acetamidine moiety. The IR and proton NMR spectra show that insertion into the metal—carbon bond has taken place. Thus the bands at ca. 2100 cm^{-1} in the spectra of the pure carbodiimides [ν_{as}(N=C=N)] are absent and additional bands are present in the 1500—1650 cm^{-1} region attributable to $C\overset{...}{-}N$ stretching modes (Tables 2—4) are present. Other complexes containing $C\overset{...}{-}N$ groups show bands in this region [7, 8]. The complexes show no bands in the 450—

TABLE 2

NMR (τ, ppm) AND IR (cm^{-1}) SPECTRA OF COMPLEXES DERIVED FROM PRCD

Complex [a]	Proton resonances [b]						
	CH [c]	Me_2C [d]	MeC	MeM	ν(M—C)	$\nu(\mathrm{C{\cdots}N})$	
$NbCl_4[PR]$	5.65	8.41	7.69			1640 m,	1508 w-m
$TaCl_4[PR]$	5.36	8.43	7.75			1645 w,	1505 m
$MeNbCl_3[PR]$	5.61	8.57	7.68	6.67	479 s	1640 m,	1542 m
$MeTaCl_3[PR]$	5.49	8.58	7.73	7.56	476 s	1646 w-m,	1518 m
$TaCl_3[PR]_2$	5.18	8.59	7.71			1644 m, 1529 m	1596 w-m,
$Me_2NbCl_2[PR]$	5.71	8.58	7.75	7.83	485 s, 463 (sh)	1640 m,	1580 w
$Me_2TaCl_2[PR]$	5.48	8.65	7.75	8.42	488 s (br)	1642 m,	1505 w
$MeTaCl_2[PR]_2$	5.55	8.66	7.84	8.89	476 w	1649 m, 1531 m	1590 w,

[a] PR = [N-i-Pr—C(Me)=N-i-Pr]. [b] Dichloromethane solution. The integrated intensities were consistent with the formulations. [c] Septet. [d] Doublet.

TABLE 3

NMR (τ, ppm) AND IR (cm^{-1}) SPECTRA OF COMPLEXES DERIVED FROM CCD

Complex [a]	Proton resonances [b]						
	CH [c]	MeC	MeM	ν(M—C)	$\nu(\mathrm{C{\cdots}N})$		
$NbCl_4[CY]$	6.02	7 69			1641 w-m,	1510 w	
$TaCl_4[CY]$	5.85	7.69			1635 m,	1506 w-m	
$MeNbCl_3[CY]$	6.20	7.66	6.67	475 s	1643 m,	1575 w,	1518 m-s
$MeTaCl_3[CY]$	5.95	7 55	7.70	471 s	1640 m,	1518 m-s	
$Me_2NbCl_2[CY]$	6.31	7.77	7.82	495 s (br)	1647 m,	1580 w-m	
$MeNbCl_2[CY]_2$	6.29	7.88	*d*	463 s	1635 m,	1548 s (br)	
$Me_2TaCl_2[CY]$	6.00	7.70	*d*	490 s, 450 m	1641 m-s,	1580 m	
$MeTaCl_2[CY]_2$	6.11	7.82	*d*	475 m	1646 w,	1624 w, 1543 s	1560 s,

[a] [CY] = [NC_6H_{11}—C(Me)=NC_6H_{11}], C_6H_{11} = cyclohexyl. [b] Dichloromethane solution. The integrated intensities were consistent with the formulations. All the complexes showed a broad group of resonance at τ 7.9—9.3 ppm attributable to the cyclohexyl groups. [c] Broad resonance. [d] Obscured by resonances of cyclohexyl group.

TABLE 4

NMR (τ, ppm) AND IR (cm^{-1}) SPECTRA OF COMPLEXES DERIVED FROM PTCD

Complex [a]	Proton resonances [b]				
	Me—aryl	MeC	MeM	ν(M—C)	$\nu(\mathrm{C{\cdots}N})$ [c]
$NbCl_4[PT]$	7.54	7.94			1633 w
$TaCl_4[PT]$	7.53	7.93			1635 w
$MeNbCl_3[PT]$	7.58	7.87	6.96	481 m	1637 m
$MeTaCl_3[PT]$	7.57	7.92	7.81	487 m	1633 m-w
$Me_2TaCl_2[PT]$	7.65	8.00	8.34	468 m	1639 w
$MeTaCl_2[PT]_2$	7.61	8.21	9.01	484 m	1641 s

[a] [PT] = [N(*p* tolyl)—C(Me)=N(*p* tolyl)]. [b] Dichloromethane solutions. The integrated intensities were consistent with the formulations of the complexes. All the complexes showed resonances at ca. τ 2.8 attributable to the aryl groups. [c] Assignments incomplete because of absorptions of aromatic rings in 1500—1600 cm^{-1} region.

550 cm^{-1} region attributable to metal—carbon stretches and moreover the resonance in the proton NMR spectrum attributable to the methyl group (ca. τ 7.7 ppm) is not in the region associated with $MeNbCl_4$ and $MeTaCl_4$ coordination complexes (τ 6.5—6.8 and τ 7.2—7.6 ppm respectively) [9, 10] but close to that found for related complexes such as MCl_4[NR—C(Me)=O] (ca. τ 7.7 ppm) [2] which is consistent with the mode of insertion proposed above.

(b). Reactions with Me_2MCl_3

Both Me_2NbCl_3 and Me_2TaCl_3 react with PRCD, CCD and PTCD yielding complexes of the type $MeMCl_3$[NR—C(Me)=NR] if an excess of Me_2MCl_3 is used. The same products are obtained if a 1/3 Me_2MCl_3/carbodiimide mole ratio and a short (< 1 h) reaction time is used, but the complex $TaCl_3$[N-i-Pr—C(Me)=N-i-Pr$]_2$ could be obtained by using excess PRCD and a longer reaction time in CH_2Cl_2 solution. The analogous reaction with Me_2NbCl_3 did not yield an analytically pure product but the proton NMR spectrum indicated that reaction with the methylmetal group had taken place. The IR and proton NMR spectra of the products derived from Me_2MCl_3 were similar to those discussed above for the $MeMCl_4$ reaction indicating a similar mode of insertion. The complexes which retained a methylmetal group showed ν(M—C) in the expected region (Tables 2—4) [9, 10].

(c). Reactions with Me_3MCl_2

The alkyls Me_3MCl_2 reacted quite readily with the carbodiimides PRCD, CCD and PTCD yielding complexes analogous to those described above. The reaction between the carbodiimide and an excess of Me_3MCl_2 yielded complexes of stoichiometry Me_2MCl_2[NR—C(Me)=NR] except for the reaction between Me_3NbCl_2 and PTCD which gave a product which was always contaminated with some $MeNbCl_2$[NR—C(Me)=NR$]_2$. When the reactions were carried out using larger quantities of the carbodiimide the behaviour of Me_3NbCl_2 and Me_3TaCl_2 differs somewhat. Thus if Me_3TaCl_2 is reacted with a small excess of PRCD, CCD or PTCD (Me_3TaCl_2/carbodiimide = 1/3) complexes of the type Me_3TaCl_2[NR—C(Me)=NR$]_2$ are obtained. The reaction between Me_3NbCl_2 and PRCD, even using a five-fold excess of PRCD, yields only the 1/1 product but the reaction between Me_3NbCl_2 and CCD (1/6 mole ratio) yields $MeNbCl_2$[NR—C(Me)=NR$]_2$ (R = cyclohexyl). The analogous tantalum complex can be obtained even when using only a 1/2 Me_3TaCl_2/CCD mole ratio of reactants, suggesting that despite the greater thermal lability of methyl—niobium as compared to methyl—tantalum bonds [9, 10], Me_3TaCl_2 is somewhat more reactive towards carbodiimides than Me_3NbCl_2.

The remaining MeTa bond in the complex $MeTaCl_2$[N-i-Pr—C(Me)=N-i-Pr$]_2$ did not react with further PRCD even when refluxed with a ten-fold excess of PRCD in CH_2Cl_2 for 16 h. A similar inertness has been observed in the reactions of Me_3TaCl_2 with NO and PhNCO [2, 3].

The IR and proton NMR spectra of the products derived from Me_3MCl_2 confirmed that the mode of insertion was analogous to that described for the reactions of $MeMCl_4$ and Me_2MCl_3. The complexes Me_2MCl_2[NR—C(Me)=NR] showed (Tables 2, 3) a rather broad band in the metal—carbon stretching region suggesting that the methyl groups are in a *cis* rather than a *trans* conformation. The proton resonance attributable to the methylmetal group in the complexes derived from both Me_2MCl_3 and Me_3MCl_2 is at a higher field than the methyl resonance of the parent alkyls [9, 10].

The complexes $MCl_4[NR—C(Me)=NR]$, $MeMCl_3[NR—C(Me)=NR]$ and $Me_2MCl_2[NR—C(Me)=NR]$ are presumably six-coordinate while the complexes $TaCl_3[N\text{-}i\text{-}Pr—C(Me)=N\text{-}i\text{-}Pr]_2$ and $MeTaCl_2[NC_6H_{11}—C(Me)=NC_6H_{11}]_2$ (C_6H_{11} = cyclohexyl) have been shown by single crystal X-ray studies to be seven-coordinate monomers containing bidentate acetamidine groups [11]; the other complexes $MeMCl_2[NR—C(Me)=NR]_2$ are thus presumably also seven-coordinate. The C—N bond distances in the chelate rings show that each C—N bond has appreciable double bond character. The IR spectra of the complexes (Tables 2—4) as discussed earlier are consistent with the partial double bond character of the C—N bonds. The complexes containing two acetamidine groups show three or four bands in the $C\overset{\cdot\cdot}{-}N$ stretching region while those containing only one group, in general show only two bands. Bands attributable to metal—nitrogen stretching modes could not be located with certainty but all the complexes showed rather complex metal—chlorine stretching modes in the 300—400 cm^{-1} region.

The reactivity of the carbodiimides PRCD, CCD and PTCD towards a particular alkyl were very similar but the analogous reactions between BUCD and Me_3TaCl_2 and Me_2NbCl_3 gave only traces of products after several days reaction at room temperature. tert-Butyl isothiocyanate and isopropyl isothiocyanate have been found to be much less reactive than MeNCS towards Me_2NbCl_3 [11], confirming that the bulk of the unsaturated reagent plays a considerable part in determining the relative ease of the insertion reaction.

The reactivities of the alkyls towards a particular carbodiimide followed the sequence, $MeMCl_4 > Me_2MCl_3 > Me_3MCl_2$, which is the same as has been observed for related reactions with RNCO and RNCS [1, 2] which is again consistent with the insertion reaction proceeding via initial formation of a donor—acceptor complex. The similar reactivites of CCD and PTCD noted above suggests that the different reactivities of PhNCX and MeNCX (X = O, S) [1, 2] arises from steric rather than electronic effects as the bulk of the cyclohexyl and *p*-tolyl groups are similar.

As the heterocumulenes RNCO, RNCS and RNCNR readily insert into Nb—C and Ta—C bonds it was of interest to see if these reactions could be extended to other related unsaturated reagents. Reactions of diphenylketene, allene, azobenzene and an imine have been investigated. Although diphenylketene reacted with $MeNbCl_4$ and $MeTaCl_4$ at room temperature pure products were not obtained; oxygen abstraction, which is a common feature of niobium and tantalum chemistry [12], probably taking place. Allene does not react with Me_2NbCl_3 or Me_3TaCl_2 at room temperature while the imine PhCH=NPh brings about reduction of $MeNbCl_4$. Reaction of $MeNbCl_4$ or $MeTaCl_4$ with azobenzene leads to the formation of a weak complex; azobenzene could be recovered unchanged after hydrolysis of the complex indicating that insertion had not taken place.

Experimental

Analyses were carried out as previously described [9]. Proton NMR spectra were measured using a Perkin—Elmer R12B instrument, IR spectra (4000—250 cm^{-1}) were recorded using Perkin—Elmer 257, 457 or 577 instruments as Nujol or hexachlorobutadiene mulls supported between KBr or polythene plates.

All manipulations were carried out in vacuo or in an atmosphere of dry oxygen free nitrogen. Solvents were dried by standard procedures. *N,N'*-di-tert-butylcarbodiimide was prepared from *N,N'*-di-tert-butylthiourea by the published procedure [13—15]. The other carbodiimides were obtained from commercial sources (iso-propyl from Aldrich, cyclohexyl from Koch—Light, and *p*-tolyl from Ralph Emanuel) and dried by prolonged pumping or with molecular sieves (4Å).

Solutions of the alkyls Me_xMCl_{5-x} (M = Nb, Ta, x = 1—3) were prepared by published methods [9, 10, 16]. Solutions of $MeMCl_4$, M = Nb, Ta in CH_2Cl_2 were prepared by the following method. A mixture of MCl_5 (0.01 mol), Me_2Zn (0.0045 mol) and CH_2Cl_2 (30 ml) was shaken for 4 h at room temperature. Unreacted MCl_5 and $ZnCl_2$ were removed by filtration and the resulting solution reacted immediately with the appropriate carbodiimide. The solution contained only $MeMCl_4$ and was not contaminated with significant quantities of other alkyls. The quantities used in the reactions described below are based on the quantity of MCl_5 used in the preparation.

Preparation of $MCl_3[NR—C(Me)=NR]$ (M = Nb, Ta, R = i-Pr, cyclohexyl, p-tolyl)

A solution of the carbodiimide (0.01 mol) in CH_2Cl_2 (20 ml) was added to a solution of $MeMCl_4$ (0.01 mol) in CH_2Cl_2 (20 ml). The solvent was removed from the reaction mixture, the solid product washed with pentane and pumped dry.

Preparation of $MeNbCl_3[NR—C(Me)=NR]$ (R = i-Pr, cyclohexyl, p-tolyl)

A solution of the carbodiimide (0.01 mol) in pentane (40 ml) was added to a solution of Me_2NbCl_3 (0.01 mol) in pentane (20 ml) at 0°. The mixture was stirred for 1 h at room temperature and the solid isolated by filtration, washed with pentane and pumped dry.

Preparation of $MeTaCl_3[NR—C(Me)=NR]$ (R = i-Pr, cyclohexyl, p-tolyl)

As above, but using 0.005 mol of the carbodiimide.

Preparation of $TaCl_3[N\text{-}i\text{-}Pr—C(Me)=N\text{-}i\text{-}Pr]_2$

$MeTaCl_3[N\text{-}i\text{-}Pr—C(Me)=N\text{-}i\text{-}Pr]$ (0.01 mol) was allowed to react with PRCD (0.06 mol) in CH_2Cl_2 (30 ml) for 12 h at room temperature. The solvent and excess ligand were removed at the pump and the residual solid extracted with pentane to remove final traces of the carbodiimide.

Preparation of $Me_2NbCl_2[N\text{-}i\text{-}Pr—C(Me)=N\text{-}i\text{-}Pr]$

A solution of PRCD (0.005 mol) in pentane (20 ml) was added to a solution of Me_3NbCl_2 (0.01 mol) in pentane at 0°. The mixture was stirred at 0° and the solid product, isolated by filtration, washed with pentane and pumped at 0°.

Preparation of $Me_2NbCl_2[NC_6H_{11}—C(Me)=NC_6H_{11}]$

A solution of *N,N'*-dicyclohexylcarbodiimide (0.006 mol) in pentane (30 ml) was added to a solution of Me_3NbCl_2 (0.01 mol) in pentane (20 ml) at 0°. The mixture was stirred for 3 h at 0° and the solid product isolated as above.

Preparation of $Me_2TaCl_2[NR{-}C(Me){=}NR]$ *(R = i-Pr, cyclohexyl, p-tolyl)*

A solution of the carbodiimide (0.005 mol) in pentane (40 ml) was added to a solution of Me_3TaCl_2 (0.01 mol) in pentane (20 ml) at 0° and the mixture stirred at room temperature for 2 h.

Preparation of $MeNbCl_2[NC_6H_{11}{-}C(Me){=}NC_6H_{11}]_2$

A solution of *N,N'*-dicyclohexylcarbodiimide (0.06 mol) in pentane (80 ml) was added to a solution of Me_3NbCl_2 (0.01 mol) in pentane at 0°. The mixture was left to stand overnight. The solid product isolated by filtration and traces of unreacted carbodiimide removed by extraction with pentane.

Preparation of $MeTaCl_2[N\text{-}i\text{-}Pr{-}C(Me){=}N\text{-}i\text{-}Pr]_2$

A mixture of PRCD (0.05 mol) and Me_3TaCl_2 (0.01 mol) in CH_2Cl_2 (20 ml) was allowed to react for 3 h at room temperature. The solvent was removed from the mixture and pentane (40 ml) added. The solid was isolated by filtration and extracted with pentane to remove the final traces of the carbodiimide.

Preparation of $MeTaCl_2[NR{-}C(Me){=}NR]_2$ *(R = cyclohexyl, p-tolyl)*

A solution of the carbodiimide (0.03 mol) in pentane (40 ml) was added to a solution of Me_3TaCl_2 (0.01 mol) in pentane (20 ml) at room temperature and stirred for 2 h. The solid product was isolated by filtration, washed with pentane and pumped dry.

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References

1 J.D Wilkins, J. Organometal. Chem., 65 (1974) 383.
2 J.D. Wilkins, J. Organometal Chem., 67 (1974) 269.
3 M.G.B. Drew and J D. Wilkins, J. Organometal. Chem., 69 (1974) 111.
4 M.S Krarasch and O. Reinmuth, Grignard reactions of non-metallic substances, Constable, London, 1954
5 M.F. Lappert and B. Prokai, Advan. Organometal. Chem., 5 (1967) 225.
6 G. Chandra, A.D. Jenkins, M.F Lappert and R.C. Srivastava, J. Chem. Soc. A, (1970) 2550.
7 J. Miller, A.L. Balch and J.H. Enemark, J. Amer. Chem. Soc., 93 (1971) 4612.
8 L.J. Bellamy, The infra-red spectra of complex molecules, Methuen, London, 1966.
9 G.W.A. Fowles, D.A Rice and J.D. Wilkins, J. Chem. Soc. Dalton Trans., (1972) 2313.
10 G.W.A. Fowles, D.A. Rice and J.D. Wilkins, J. Chem. Soc. Dalton Trans., (1973) 961.
11 M.G.B. Drew and J.D Wilkins, in the press.
12 F. Fairbrother, The chemistry of niobium and tantalum, Elsevier, Amsterdam, 1967.
13 M. L. Moore and F.S. Crossley, Org. Syn. Coll. Vol., 3 (1955) 559.
14 M.L. Moore and F.S. Crossley, Org. Syn. Coll. Vol., 3 (1955) 617.
15 P. Schlack and G. Keil, Justus Liebigs Ann. Chem., 661 (1963) 164.
16 G.W.A. Fowles, D.A. Rice and J.D. Wilkins, J. Chem. Soc. Dalton Trans., (1974) 1080