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Reactions of $(\eta^5\text{-}C_5Me_5)Ta(PMe_3)(H)_2(\eta^2\text{-}CHPMe_2)$ with heterocumulenes and the interconversion of tautomeric formamido complexes of tantalum

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Abstract

The complex $(\eta^5\text{-}C_5Me_5)Ta(PMe_3)(H)_2(\eta^2\text{-}CHPMe_2)$ (**1**) reacts with aryl isocyanates, RNCO ($R = C_6H_5$, $4\text{-}MeC_6H_4$) to afford the hydrido-formamido complexes $(\eta^5\text{-}C_5Me_5)Ta(H)(\eta\text{-}OCHNR)(\eta^2\text{-}CHPMe_2)$ ($R = C_6H_5$ (**2**), $4\text{-}MeC_6H_4$ (**3**)) which exist in two tautomeric forms in solution. The interconversion of these isomers proceeds *via* an intramolecular rotation of the (OCHNR) moiety analogous to the equilibration of *syn* and *anti* hydrogens of an η^3-allyl ligand. Compound **1** undergoes insertion of two equivalents of CO_2 to afford $(\eta^5\text{-}C_5Me_5)Ta(\eta^1\text{-}OCHO)(\eta^2\text{-}CHPMe_2)$ (**4**), a complex containing η^1 and η^2-formamato ligands.

Key words: Tantalum; Heterocumulenes; Formamido; Isocyanate; Fluxionality

1. Introduction

During our studies on the cyclometallated complex $(\eta^5\text{-}C_5Me_5)Ta(PMe_3)(H)_2(\eta^2\text{-}CHPMe_2)$ (**1**) we noted the ease with which olefins insert into the metal hydride bonds to afford coordinatively unsaturated dialkyls and how modification of the ligand field may be exploited to obtain selective catalytic dimerization of ethylene to but-1-ene [1]. Subsequently, we investigated the reactions of **1** with other unsaturated organic substrates and here report on the interactions between **1** and the heterocumulenes RNCO ($R = C_6H_5$, $4\text{-}MeC_6H_4$) and CO_2.

2. Results and discussion

One equivalent of RNCO reacts smoothly with **1** in toluene at room temperature to afford hydrido-formamido complexes of formula $(\eta^5\text{-}C_5Me_5)Ta(H)(\eta\text{-}OCHNR)(\eta^2\text{-}CHPMe_2)$ ($R = C_6H_5$ (**2**), $4\text{-}MeC_6H_4$ (**3**)) (Scheme 1). Infrared spectroscopy reveals the presence of a single hydrido ligand which absorbs at 1738 cm^{-1} for both **2** and **3**, whilst bands centred at 1560 cm^{-1} and 1550 cm^{-1}, respectively, are indicative of chelating formamido ligands [2]. The $(\eta^2\text{-}CHPMe_2)$ moiety remains intact during the transformation and one equivalent of PMe_3 is liberated (as indicated by ^1H NMR spectroscopy). Monitoring the progress of reaction by ^1H NMR spectroscopy did not reveal any detectable intermediates.

Both **2** and **3** show temperature-dependent solution NMR behaviour. The room temperature ^1H NMR spectrum of **2** (C_6D_6) reveals the presence of two isomeric hydride complexes with the metal-bound hydrogens resonating at 12.79 ppm and 11.68 ppm and displaying coupling to a single phosphorus nucleus. The ratio of these two signals is approximately 3 : 7, which is in agreement with the ratio of the ^{31}P resonances for the η^2-$CHPMe_2$ ligand. Additionally, resonances assignable to two distinct formamide groups can also be observed in both the ^1H and $^{13}C\{^1H\}$ NMR spectra, the formamido hydrogens appearing at 9.01 ppm and 8.76 ppm and the formamido carbons at 168.88 ppm and 166.61 ppm (Table 1); these shifts are comparable to those found for related formamido complexes [2].

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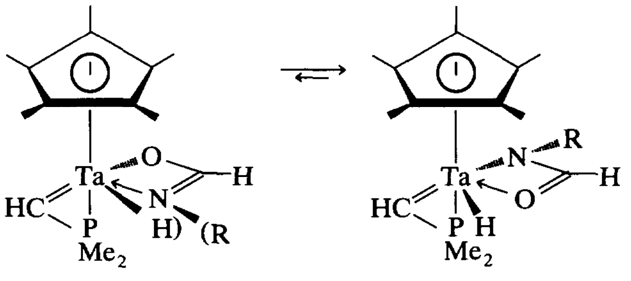
TABLE 1. $^{13}C\{^1H\}$ NMR data for **2** in benzene-d_6 at 298 K

Shift (ppm) [a]	Multiplicity	J (Hz)	Assignment
206.17	d	$^1J(PC) = 56.0$	M=*C*H
168.88	s		PhN*C*HO
166.61	s	–	PhN*C*HO
144.64	s	–	Ph–C_{ipso}
124.10	s	–	Ph
120.95	s	–	Ph
113.15	s	–	C_5Me_5
20.26	d	$^1J(PC) = 27.3$	P*Me*$_2$
13.10	s, br	–	P*Me*$_2$
11.63	s	–	C_5*Me*$_5$

[a] One of the phenyl resonances is obscured by the solvent.

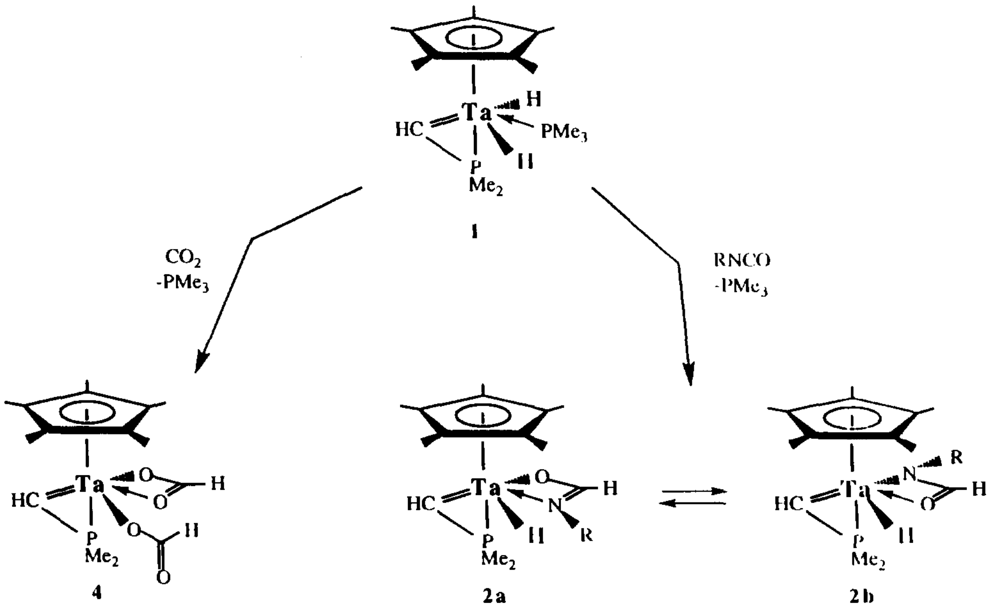
The ^1H NMR of **2** has been studied over the temperature range 275–335 K in C_7D_8 solvent and the limiting spectra are reproduced in Fig. 1. At the high temperature limit (temperatures above 335 K lead to decomposition) a single set of resonances is observed for the hydride and formamido hydrogen environments, implying rapid exchange on the NMR timescale (Fig. 1(a)). Below 295 K, distinct signals are observed for the formamido and hydride sites of each isomer (Fig. 1(b), Table 2).

On the basis of our previous observations on the (η^5-C_5Me_5)Ta(PMe_3)(H)$_2$(η^2-$CHPMe_2$) system [1,3], reasonable geometries for the two isomers are those containing chelating formamido ligands with either O or N *trans* to the hydride ligand, as illustrated in Scheme 1. There is no unambiguous evidence to indicate which of the two forms predominates in solution; however, in the hydrido-halide derivatives (η^5-C_5Me_5)Ta(PMe_3)(H)(X)(η^2-$CHPMe_2$) (X = Cl, Br, I) we have observed that the chemical shift of the metal hydride ligand is strongly dependent upon the electronegativity of the ligand X; the more electronegative this group, the higher is the frequency of the hydride resonance [3]. Since oxygen is more electronegative than nitrogen [4], isomer **2a**, with a transoid oxygen atom, is expected to show the higher frequency hydride signal, and from the low temperature ^1H NMR spectrum, the equilibrium constant *K* between the isomers is *ca.* 1.6 (in favour of **2b**) which translates to a free-energy difference (ΔG) of *ca.* 0.9 kJ mol^{-1} (at 225 K). The ground state preference for **2b** is most likely to be a consequence of unfavourable steric interactions between the formamido phenyl substituent and the metal hydride ligand as shown below, although the energy difference between the tautomers is relatively small.



2a **2b**

Formation of **2a** and **2b** most reasonably proceeds *via* insertion of aryl isocyanate into the tantalum-hydride bond, as shown in Scheme 2, followed by rotation about the N–C bond of the incipient η^1-formamido



Scheme 1. Reactions of **1** with arylisocyanates (R = C_6H_5, **2**; 4-MeC_6H_4, **3**) and carbon dioxide.

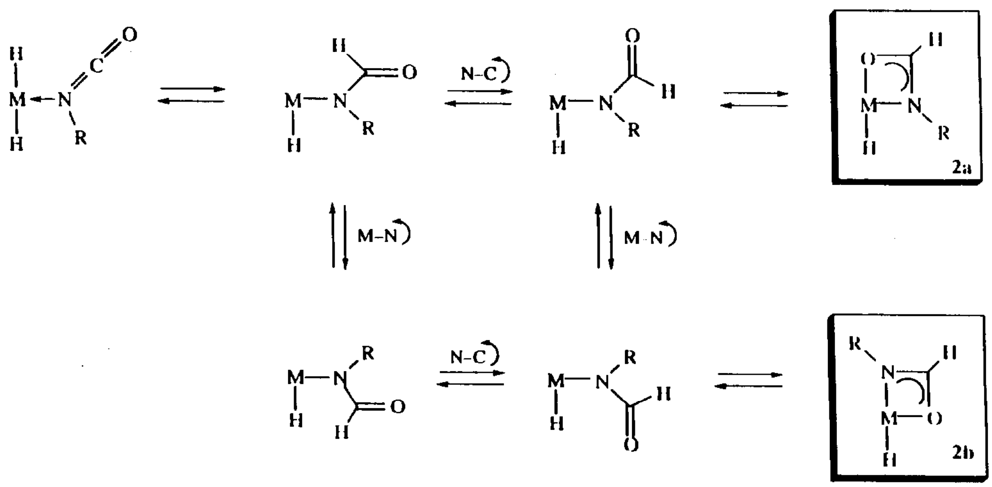
TABLE 2. ^1H NMR data for **2a** and **2b** in toluene-d_8 at 235 K

Compound	Shift (ppm) [a]	Rel. Int.	Multiplicity	J (Hz)	Assignment
2a	12.54	1	d	$^2J(PH) = 35.6$	M-*H*
	9.09	1	d	$^2J(PH) = 3.2$	M=C*H*
	8.71	1	d	–	PhNC*H*O
	1.84	15	s	–	C_5Me_5
	1.60	3	d	$^2J(PH) = 10.1$	PMe_2
	1.24	3	d	$^2J(PH) = 9.7$	PMe_2
2b	11.42	1	d	$^2J(PH) = 25.9$	M-*H*
	9.12	1	d	$^2J(PH) = 2.6$	M=C*H*
	8.47	1	s	–	PhNC*H*O
	1.84	15	s	–	C_5Me_5
	1.68	3	d	$^2J(PH) = 10.6$	PMe_2
	1.31	3	d	$^2J(PH) = 10.0$	PMe_2

[a] Phenyl hydrogens resonate between 7.3 and 6.5 ppm but were not resolved.

species and coordination of the pendant arm to give **2a**. An additional rotation, about the metal–nitrogen bond, will give rise to **2b**, and this also provides a mechanism for interconversion of the two tautomers. Such a mechanism is analogous to the equilibration of *syn* and *anti* hydrogens of an η^3-allyl ligand *via* bond rotation within an intermediate η^1-allyl complex [5]. It should be noted that the interconversion could also proceed *via* dissociation of the nitrogen arm of the formamido ligand with associated rotations about the M–O and C–O bonds. There is no evidence in favour of the reverse β-hydrogen elimination to regenerate the metal-dihydride and aryl isocyanate, at least on the timescale of the interconversion. Such a process would be expected to lead to magnetization transfer between the hydride and formamido hydrogen sites, but in spin saturation transfer experiments performed in C_7D_8 solvent at both 298 K and 253 K, saturation transfer was observed only between the two hydride sites.

Treatment of a petroleum ether solution of **1** with CO_2 (1 atm) at room temperature leads to separation of a white solid during 24 h. This compound is only sparingly soluble in common solvents, preventing meaningful NMR studies. However, elemental analysis is consistent with incorporation of two equivalents of CO_2, and the infrared spectrum reveals strong absorptions at 1565 cm^{-1} and 1650 cm^{-1} attributable to the $\nu_{as}(CO_2)$ absorptions of η^2 and η^1 formato ligands, respectively (*cf.* $MoH(\eta^2\text{-}OCHO)(PMe_3)_4$, 1570 cm^{-1} [2]; $Cu(\eta^2\text{-}OCHO)(PPh_3)_2$, 1565 cm^{-1} [6]; $Cu(\eta^1\text{-}OCHO)[(PPh_2CH_2)_3CMe]$, 1620 cm^{-1} [7] and $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}OCHO)$, 1620 cm^{-1} [8]). In addition, an absorption at 2720 cm^{-1} is assignable to the ν(CH) vibrations of the formato ligands. These data



Scheme 2. Pathways for the formation and interconversion of formamido isomers **2a** and **2b**.

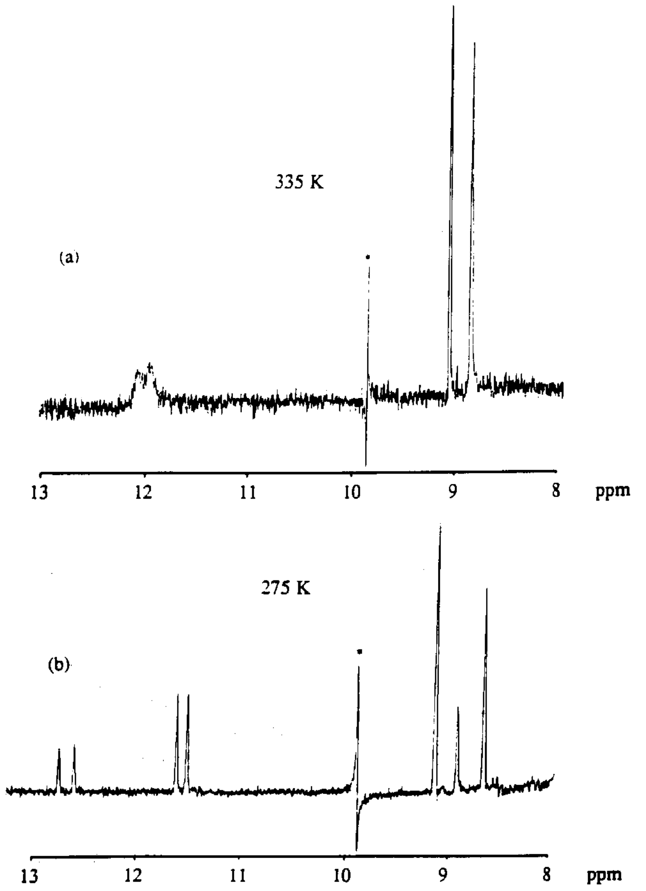


Fig. 1. Portions of the ^1H NMR spectra of **2** at (a) 335 K and (b) 275 K in C_7D_8 solvent. * indicates a folded peak. The resonance at δ 9.1 ppm contains overlapping (C*HP*Me_2) signals from both tautomers **2a** and **2b**.

indicate that CO_2 has inserted into both metal hydride bonds of **1** to afford a bis(formato) complex of the type $(\eta^5\text{-}C_5Me_5)Ta(\eta^1\text{-}OCHO)(\eta^2\text{-}OCHO)(\eta^2\text{-}CHPMe_2)$ (**4**) (Scheme 1).

3. Experimental details

All manipulations were performed on a conventional vacuum/inert atmosphere line using standard Schlenk and cannula techniques or in a nitrogen-filled dry-box. Solvents were dried by prolonged reflux and subsequent distillation from a suitable drying agent (in parentheses); toluene (sodium metal), light petroleum ether (40–60°C, lithium aluminium hydride) and dichloromethane (calcium hydride). Deuterated solvents (C_6D_6, C_7D_8, $CDCl_3$) were dried by vacuum distillation from phosphorus(V) oxide and stored over 4 Å molecular sieves. All solvents were freshly deoxygenated prior to use. Elemental analyses were performed by the Microanalytical laboratory of this department. Infrared spectra were recorded on Perkin-Elmer 577 and 457 grating spectrophotometers using either KBr or CsI windows. Absorptions are abbreviated as: s (strong), m (medium), w (weak), br (broad), sp (sharp) and sh (shoulder). Mass spectra were recorded on a VG 7070E Organic Mass Spectrometer. NMR spectra were obtained using a Bruker AC 250, with ^1H at 250.13 MHz, ^{13}C at 60.90 MHz and ^{31}P at 101.26 MHz, at ambient temperature unless stated otherwise. The following abbreviations have been used for band multiplicities: s (singlet), d (doublet), t (triplet), m (multiplet). Chemical shifts are quoted as δ in ppm with respect to the residual proton resonances in the deuterated solvents (for ^1H and ^{13}C) or to aqueous 85% H_3PO_4 for ^{31}P. Isocyanates were purified by distillation and $(\eta^5\text{-}C_5Me_5)Ta(PMe_3)(H)_2(\eta^2\text{-}CHPMe_2)$ was prepared as previously described [1].

3.1. Synthesis of $(\eta^5\text{-}C_5Me_5)Ta(H)(\eta\text{-}OCHNPh)(\eta^2\text{-}CHPMe_2)$ (2)

The isocyanate PhNCO (38 mg, 0.32 mmol) was added by syringe to a solution of $(\eta^5\text{-}C_5Me_5)Ta(PMe_3)(H)_2(\eta^2\text{-}CHPMe_2)$ (150 mg, 0.32 mmol) in toluene (20 cm^3) at room temperature. After 1 h of stirring, the solution was filtered and the clear filtrate was concentrated to 5 cm^3 and layered with cold (−35°C) light petroleum (10 cm^3). In, white solid formed immediately and was filtered off then dried *in vacuo*. Recrystallization from a toluene/petroleum ether mixture (*ca.* 1:2 v/v) afforded the product as colourless crystals. Yield 0.1 g (61%). Elemental Anal. Found: C, 46.12, H, 5.55; N, 2.42. $C_{20}H_{29}NOPTa$. calcd.: C, 46.97; H, 5.73; N, 2.74%. $^{31}P\{^1H\}$ NMR (C_6D_6): −58.26 (s), −72.23 (s). IR (Nujol, KBr): 3050w, 3025w, 1738m, 1560s, 1390m, 1270s, 1222m, 1029w, 956m, 938m, 929m, 835w, 761s, 719m, 693m, 685m, 615w cm^{-1}. MS (EI, 70 eV); *m/e* 511 $[M]^+$, 392 $[M-PhNCO]^+$.

3.2. Synthesis of $(\eta^5\text{-}C_5Me_5)Ta(H)(\eta\text{-}OCHN\{C_6H_4\text{-}4\text{-}Me\})(\eta^2\text{-}CHPMe_2)$(3)

The procedure employed was analogous to that for **2**, the following reagents: 4-MeC_6H_4NCO (140 mg, 1.07 mmol), $(\eta^5\text{-}C_5Me_5)Ta(PMe_3)(H)_2(\eta^2\text{-}CHPMe_2)$ (500 mg, 1.07 mmol) in toluene solvent (30 cm^3). Yield 0.24 g (43%). Elemental Anal. Found: C, 48.53; H, 6.23; N, 2.42. $C_{21}H_{31}NOPTa$ calcd.: C, 48.00; H, 5.96; N, 2.67%. ^1H NMR (C_6D_6): 12.81 (d, 1H, $^2J(PH) = 35.0$, M-*H*); 11.70 (d, 1H, $^2J(PH) = 26.2$, M–H); 9.17 (s, 1H, $^2J(PH) = 2.3$, M=C*H*); 9.05 (s, 1H, TolNC*H*O); 8.80 (s, 1H, TolNC*H*O); 7.2–6.5 (m, 4H, Ar-*H*); 2.12

(s, 3H, Tol-CH_3); 2.00 (s, 15H, C_5Me_5); 1.75 (d, 3H, ^2J(PH) = 11.0, PMe_2); 1.40 (d, 3H, ^2J(PH) = 10.0, PMe_2). $^{31}P\{^1H\}$ NMR (C_6D_6): −58.25 (s), −72.04 (s). IR (Nujol, CsI): 3050w, 3015w, 2720w, 1905w, 1738s, 1550s, br, 1512s, 1420m, 1318s, 1295s, 1270s, 1225s, 1110m, 1069w, 1030m, 1019m, 960s, 935s, br, 857m, 825s, 812s, 715s, 683s, 645m, 630m, br, 549m, 524m, 425w, 415w, 378s, 347m, 300m, br cm^{-1}. MS. (EI, 70 eV): 525 $[M]^+$, 406 $[M - C_6H_5NCO]^+$.

3.3. Synthesis of $(\eta^5\text{-}C_5Me_5)Ta(\eta^1\text{-}OCHO)(\eta^2\text{-}OCHO)(\eta^2\text{-}CHPMe_2)$ (4)

A petroleum ether solution of $(\eta^5\text{-}C_5Me_5)Ta(PMe_3)(H)_2(\eta^2\text{-}CHPMe_2)$ (290 mg, 0.62 mmol in 20 cm^3) was treated with 1 atm of CO_2 at room temperature. A white solid immediately separated. After 24 h the product was filtered off, washed with light petroleum ether (2 × 5 cm^3), and dried *in vacuo*. Yield 0.23 g. Elemental Anal. Found: C, 37.70; H, 5.14. $C_{15}H_{24}O_4PTa$ calcd.: C, 37.51; H, 5.05. IR (Nujol, KBr): 2720w, 2220w, 1650s, br, 1565s, br, 1420m, br, 1290m, br, 1265m, br, 1095s, br, 1030m, 955s, br, 786m, 773m, 710s, br, 545s, br cm^{-1}.

Acknowledgments

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