Zirconocene-like Reactivity of Half-sandwich Tantalum Imido Complexes: New C–C Coupling Reagents

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Half-sandwich imido tantalacyclopentane complexes are prepared *via* alkene coupling reactions: their novel insertion chemistry with CO and MeCN is reported.

In recent years zirconocene reagents have emerged as powerful synthetic tools for organic synthesis,[1] facilitating the coupling of a wide variety of unsaturated organic molecules including *inter alia* alkenes,[2,3] alkynes,[4,5] benzynes[1b,d,6] and imines.[7] They have also found widespread and technologically significant applications in the polymerisation of alkenes,[8] α,ω-dienes[9] and silanes.[10] We have been exploring the chemistry of half-sandwich imido compounds of the Group 5 metals[11] which may offer an opportunity to extend the horizon of zirconocene-like reactivity through the 'isolobal' relationship that exists between $[M(\eta\text{-}C_5R_5)(NR)]$ (M = Group 5 metal) and $[M(\eta\text{-}C_5R_5)_2$ (M = Group 4 metal) fragments.[11a] Our work to date has shown that niobium derivatives of the type $Nb(\eta\text{-}C_5R_5)(NR')(L)(PMe_3)]$ (R = H or alkyl; R' = aryl; L = alkene, alkyne, alkylidene or benzyne), while displaying many structural similarities to their metallocene analogues, do not engage in synthetically desirable oxidative C–C coupling processes due to over-zealous binding of the tertiary phosphine ligand. Teuben and co-workers have recently noted a similar effect for analogous vanadium complexes.[12]

Here, we describe a significant breakthrough in the development of Group 5 metal imido systems as potential reagents for organic transformations with the discovery that the half-sandwich tantalum imido system, unlike its lighter metal congeners, readily facilitates oxidative couplings and novel insertion processes.

A key development was the synthesis of the tantalacyclopentane complex 2 which may be obtained in high yield from $[Ta(\eta\text{-}C_5Me_5)(NC_6H_3Pr^i_2\text{-}2,6)Cl_2]$ 1[11a] upon treatment with an excess of ethylmagnesium chloride in the presence of an ethene atmosphere (Scheme 1), and may be isolated as yellow needles from concentrated diethyl ether solutions at $-78\,°C$. Complex 2 is soluble in aromatic and aliphatic hydrocarbons and indefinitely stable in chlorocarbons. NMR data† are consistent with metallacyclopentane character rather than a dialkene adduct; in particular ^{13}C NMR resonances at δ 16.20 and 53.54 due to the α and β ring carbons and with $^1J_{CH}$ coupling constants of 129 and 131 Hz, respectively, are consistent with sp^3 hybridised methylene units. Despite its metallacyclopentane character, 2 undergoes slow exchange with C_2D_4 (days at 60 °C) to give the perdeuteriated metallacycle $[^2H_8]$-2 indicating that the reverse β-C–C bond cleavage can occur, if only transiently, to generate the dialkene species.[1c] Trimethylphosphine will also displace one of the ethene groups to give the phosphine adduct 3 (Scheme 2). In behaviour reminiscent of zirconacyclopentanes,[1c] 2 does not undergo facile β-H elimination to afford but-1-ene, even upon prolonged heating at 120 °C, due to conformational constraints that prevent the C_β–H bonds from accessing the metal-centred LUMO.

Complex 2 undergoes a number of novel insertion reactions in which the C_4 fragment is retained. For example, reaction with
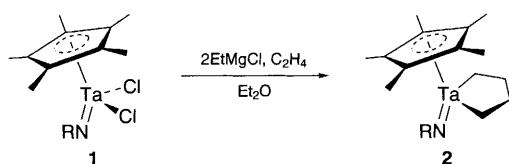
excess carbon monoxide results in the orange diacyl complex 4 in which CO has inserted into both of the metallacyclic Ta–C bonds. Monitoring of the reaction by ^1H NMR spectroscopy did not reveal any evidence for the monoacyl intermediate implying that the second insertion occurs at a rate substantially faster than the first insertion. The acyl carbons resonate at δ 133.74 in the ^{13}C NMR spectrum implying an η^1-bonding mode which again is likely to be a consequence of geometrical constraints within the metallacyclic ring. In contrast, acetonitrile inserts into just one of the Ta–C bonds of 2 to give the thermally robust azatantalacycle product 5 in high yield and with excellent regiocontrol; this is believed to be a consequence of steric factors, analogous to the effect observed in the coupling of acetonitrile with zirconocene benzynes.[1b]

Tertiary phosphine derivatives can also be used as precursors to the oxidatively coupled tantalacyclopentane products. Whereas the ethene complex 3 forms an equilibrium with the tantalacyclopentane 2 in the presence of free ethene and PMe₃, derivatives containing more highly substituted alkenes such as the propene complex 6 (Scheme 3) convert quantitatively to the metallacyclic ring products, presumably as a result of the

Scheme 2 R = C₆H₃Pri₂-2,6

2EtMgCl, C₂H₄
Et₂O
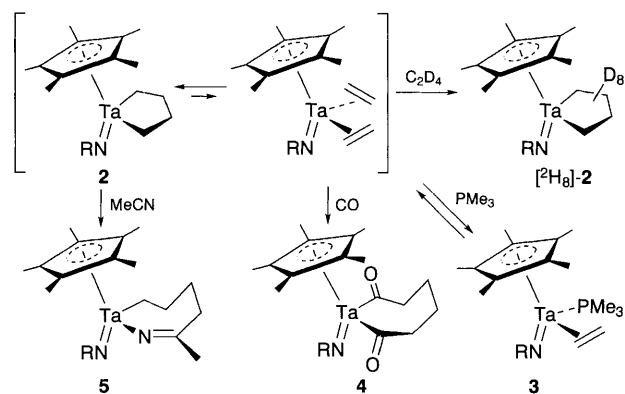
Scheme 1 R = C₆H₃Pri₂-2,6
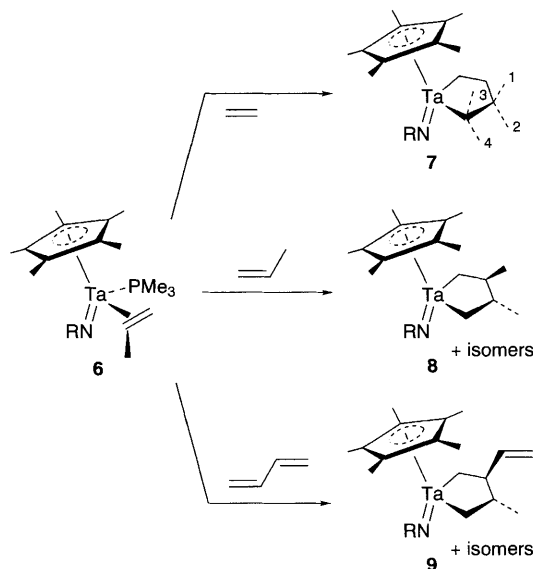
Scheme 3 R = C₆H₃Pri₂-2,6

greater steric influence of the propene methyl substituent, an effect related to the more ready displacement of but-1-ene from the zirconocene fragment.[1c] Consequently, treatment of **6** with ethene forms the methyl-substituted tantalacyclopentane complex **7**, which exists as an equimolar mixture of the four possible isomers indicating that there is no energetic preference for one form. Propene reacts to give the disubstituted tantalacyclopentane **8**, again as a mixture of isomers, though in this case two clearly predominate (by NMR). Butadiene reacts in an analogous fashion to incorporate one of its double bonds within the tantalacyclopentane ring, leaving an exocyclic vinyl group. Prolonged warming to 100 °C does not lead to expulsion of propene and formation of a butadiene complex analogous to [Zr(η-C_5H_5)(butadiene)].[13]

In summary, these results indicate the potential for novel C–C coupling and insertion reactions mediated by [Ta(η-C_5R_5)(NR)] reagents and represent an important breakthrough in the development of half-sandwich imido metal reagents for use in organic synthesis. Some potentially useful differences to zirconocene-mediated transformations are already apparent, and clear opportunities exist for tuning selectivity through both cyclopentadienyl ring and imido substituents.

Footnote

† Satisfactory elemental analyses have been obtained. *Selected spectroscopic characterising data* for **2**: ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ 0.96, 1.68, 2.22, 2.48 (complex, 8H, C_4H_8), 1.39 (d, 12H, $^3J_{HH}$ 6.8 Hz, CH*Me*$_2$), 1.73 (s, 15H, C_5Me_5), 3.74 (spt., 2H, $^3J_{HH}$ 6.8 Hz, C*H*Me$_2$), 7.00 (t, 1H, $^3J_{HH}$ 7.5 Hz, p-C_6H_3), 7.25 (d, 2H, $^3J_{HH}$ 7.5 Hz, m-C_6H_3). ^{13}C NMR (C_6D_6, 100.6 MHz, 298K): δ 10.63 (q, $^1J_{CH}$ 127 Hz, C_5Me_5), 16.20 (t, $^1J_{CH}$ 129 Hz, C_4H_8), 24.46 (q, $^1J_{CH}$ 126 Hz, CH*Me*$_2$), 28.20 (d, $^1J_{CH}$ 124 Hz, C*H*Me$_2$), 53.54 (t, $^1J_{CH}$ 131 Hz, C_4H_8), 115.92 (s, C_5Me_5), 122.19 (d, $^1J_{CH}$ 152 Hz, m-C_6H_3), 144.01 (s, o-C_6H_3), 157.70 (s, *ipso*-C_6H_3). For **3**: ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ −0.14, 0.95, 1.60 (components of AA'MM' spin pattern, 4H, C_2H_4), 1.08 (d, 9H, $^2J_{PH}$ 7.2 Hz, PMe$_3$), 1.29 (d, 6H, $^3J_{HH}$ 6.8 Hz, CH*Me*$_2$), 1.31 (d, 6H, $^3J_{HH}$ 6.8 Hz, CH*Me*$_2$), 1.78 (s, 15H, C_5Me_5), 3.94 (spt., 2H, $^3J_{HH}$ 6.8 Hz, C*H*Me$_2$), 6.96 (t, 1H, $^3J_{HH}$ 6.8 Hz, p-C_6H_3), 7.25 (d, 2H, $^3J_{HH}$ 6.8 Hz, m-C_6H_3). ^{13}C NMR (C_6D_6, 100.6 MHz, 298 K): δ 11.14 (q, $^1J_{CH}$ 126 Hz, C_5Me_5), 16.87 (qd, $^1J_{CH}$ 129, $^1J_{CP}$ 26 Hz, PMe$_3$), 24.79 (q, $^1J_{CH}$ 120 Hz, CH*Me*$_2$), 26.59 (d, $^1J_{CH}$ 130 Hz, C*H*Me$_2$), 29.61 (td, $^1J_{CH}$ 147, $^2J_{CP}$ 2 Hz, C_2H_4), 35.66 (td, $^1J_{CH}$ 149, $^2J_{CP}$ 11 Hz, C_2H_4), 108.65 (s, C_5Me_5), 120.74 (d, $^1J_{CH}$ 159 Hz, p-C_6H_3), 122.57 (d, $^1J_{CH}$ 153 Hz, m-C_6H_3), 142.70 (s, o-C_6H_3), 153.00 (s, *ipso*-C_6H_3). For **4**: ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ 1.29 (d, 12H, $^3J_{HH}$ 6.9 Hz, CH*Me*$_2$), 1.40, 1.65, 2.35, 2.65 [m, 8H, C(O)C_4H_8C(O)], 1.96 (s, 15H, C_5Me_5), 3.52 (spt., 2H, $^3J_{HH}$ 6.9 Hz, C*H*Me$_2$), 6.66 (t, 1H, $^3J_{HH}$ 7.8 Hz, p-C_6H_3), 7.13 (d, 2H, $^3J_{HH}$ 7.8 Hz, m-C_6H_3). ^{13}C NMR (C_6D_6, 100.6 MHz, 298 K): δ 10.44 (q, $^1J_{CH}$ 128 Hz, C_5Me_5), 23.03 [t, $^1J_{CH}$ 128, C(O)C_4H_8C(O)], 24.30 (q, $^1J_{CH}$ 126 Hz, CH*Me*$_2$), 27.40 (d, $^1J_{CH}$ 125 Hz, C*H*Me$_2$), 28.94 [t, $^1J_{CH}$ 131, C(O)C_4H_8C(O)], 118.79 (s, C_5Me_5), 121.03 (d, $^1J_{CH}$ 157 Hz, p-C_6H_3), 122.11 (d, $^1J_{CH}$ 153 Hz, m-C_6H_3), 133.74 [s, C(O)C_4H_8C(O)], 141.11 (s, o-C_6H_3), 150.86 (s, *ipso*-C_6H_3). For **5**: ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ 1.33 (d, 6H, $^3J_{HH}$ Hz, CH*Me*$_2$), 1.41 (d, 6H, $^3J_{HH}$ Hz, CH*Me*$_2$), 1.60 [s, 3H, N=C(*Me*)], 1.83 (s, 15H, C_5Me_5), 0.90, 2.3, 2.5 (m, metallacycle CH$_2$'s). ^{13}C NMR (C_6D_6, 100.6 MHz, 298 K): δ 10.87 (C_5Me_5), 24.15 (CH*Me*$_2$), 24.21 (C*H*Me$_2$), 28.02 (C*H*Me$_2$), 28.47 [(N=C(*Me*)], 28.86, 30.40, 42.76, 45.20 (metallacycle CH$_2$'s), 114.94 (C_5Me_5), 184.62 [N=C(Me)].

References

1 For recent reviews, see: (*a*) E. Negishi in *Comprehensive Organic Synthesis*, ed. L. Paquette, Pergamon, New York, 1991, vol. 5, p. 1163;

(*b*) S. L. Buchwald and R. B. Nielsen, *Chem. Rev.*, 1988, **88**, 1047; (*c*) E. Negishi and T. Takahashi, *Acc. Chem. Res.*, 1994, **27**, 124; (*d*) R. D. Broene and S. L. Buchwald, *Science*, 1993, **261**, 1696.

2 S. L. Buchwald, B. T. Watson and J. C. Huffman, *J. Am. Chem. Soc.*, 1986, **108**, 7411; 1987, **109**, 2544; S. L. Buchwald, R. T. Lum and J. C. Dewan, *J. Am. Chem. Soc.*, 1986, **108**, 7441; W. A. Nugent and D. F. Taber, *J. Am. Chem. Soc*., 1989, **111**, 6435; T. Takahashi, M. Kageyama, V. Denisov, R. Hara and E. Negishi, *Tetrahedron Lett.*, 1993, **34**, 687; C. Copéret, E. Negishi, Z. Xi and T. Takahashi, *Tetrahedron Lett.*, 1994, **35**, 695; T. Takahashi, N. Suzuki, M. Hasegawa, Y. Nitto, K. Aoyagi and M. Saburi, *Chem. Lett.*, 1992, 331.

3 For alkene coupling plus carbomagnesiation, see: T. Takahashi, T. Seki, Y. Nitto, M. Saburi, C. J. Rousset and E. Negishi, *J. Am. Chem. Soc.*, 1991, **113**, 6266; K. S. Knight and R. M. Waymouth, *J. Am. Chem. Soc.*, 1991, **113**, 6268; D. P. Lewis, P. M. Muller, R. J. Whitby and R. V. H. Jones, *Tetrahedron Lett.*, 1991, **32**, 7735; U. Wischmeyer, K. S. Knight and R. M. Waymouth, *Tetrahedron Lett.*, 1992, **33**, 6797; A. Hoveyda, J. P. Morken and A. F. Houri, *J. Am. Chem. Soc.*, 1992, **114**, 6692; J. P. Morken, M. T. Didiuk and A. Hoveyda, *J. Am. Chem. Soc.*, 1993, **115**, 6997; K. S. Knight, D. Wang, R. M. Waymouth and J. Ziller, *J. Am. Chem. Soc.*, 1994, **116**, 1845.

4 B. P. Warner, W. M. Davis and S. L. Buchwald, *J. Am. Chem. Soc.*, 1994, **116**, 5471.

5 For bicyclisations of enynes and diynes see: E. Negishi, S. J. Holmes, J. M. Tour and J. A. Miller, *J. Am. Chem. Soc.*, 1985, **107**, 2568; E. Negishi, D. R. Swanson, F. E. Cederbaum and T. Takahashi, *Tetrahedron Lett.*, 1987, **28**, 917; E. Negishi, H. Sawada, J. M. Tour and Y. Wei, *J. Org. Chem.*, 1988, **53**, 913; E. Negishi, S. J. Holmes, J. M. Tour, J. A. Miller, F. E. Cederbaum, D. R. Swanson and T. Takahashi, *J. Am. Chem. Soc.*, 1989, **111**, 3336; W. A. Nugent, D. L. Thorn and R. L. Harlow, *J. Am. Chem. Soc.*, 1987, **109**, 2788; P. J. Fagan and W. A. Nugent, *J. Am. Chem. Soc.*, 1988, **110**, 2310; T. V. Rajanbabu, W. A. Nugent, D. F. Taber and P. J. Fagan, *J. Am. Chem. Soc.*, 1988, **110**, 7128; E. Negishi, F. E. Cederbaum and T. Takahashi, *Tetrahedron Lett.*, 1986, **27**, 2829.

6 J. H. Tidwell, D. R. Senn and S. L. Buchwald, *J. Am. Chem. Soc.*, 1991, **113**, 4685; J. H. Tidwell and S. L. Buchwald, *J. Org. Chem.*, 1992, **57**, 6380; *J. Am. Chem. Soc.*, 1994, **116**, 11797.

7 S. L. Buchwald, B. T. Watson, M. W. Wannamaker and J. C. Dewan, *J. Am. Chem. Soc.*, 1989, **111**, 4486; N. Coles, R. J. Whitby and J. Blagg, *Synlett*, 1990, 271; N. Coles, M. C. J. Harris, R. J. Whitby and J. Blagg, *Organometallics*, 1994, **13**, 190.

8 For recent reviews of acyclic alkene polymerisation, see R. F. Jordan, *Adv. Organomet. Chem.*, 1991, **32**, 325, and references therein; W. Kaminsky, *Catal. Today*, 1994, **20**, 257, and references therein. For cyclic alkene polymerisation, see W. Kaminsky, R. Bark, R. Spiehl, N. Moller-Lindenhof and S. Niedoba, *Transition Metals and Organometallics as Catalysts for Olefin Polymerisation*, ed. W. Kaminsky and H. Sinn, Springer-Verlag: Berlin, 1988, pp. 291–301; S. Collins and W. M. Kelly, *Macromolecules*, 1992, **25**, 233; W. M. Kelly, N. J. Taylor and S. Collins, *Macromolecules*, 1994, **27**, 4477.

9 L. Resconi and R. M. Waymouth, *J. Am. Chem. Soc.*, 1990, **112**, 4953; G. W. Coates and R. M. Waymouth, *J. Am. Chem. Soc.*, 1991, **113**, 6270.

10 T. D. Tilley, *Acc. Chem. Res.*, 1993, **26**, 22, and references therein; S. Bourg, R. J. P. Corriu, M. Enders and J. J. E. Moreau, *Organometallics*, 1995, **14**, 564.

11 (*a*) D. N. Williams, J. P. Mitchell, A. D. Poole, U. Siemeling, W. Clegg, D. C. R. Hockless, P. A. O'Neil and V. C. Gibson, *J. Chem. Soc., Dalton Trans.*, 1992, 739; (*b*) A. D. Poole, V. C. Gibson and W. Clegg, *J. Chem. Soc., Chem. Commun.*, 1992, 237; (*c*) U. Siemeling and V. C. Gibson, *J. Organomet. Chem.*, 1992, **426**, C25; (*d*) J. K. Cockcroft, V. C. Gibson, J. A. K. Howard, A. D. Poole, U. Siemeling and C. Wilson, *J. Chem. Soc., Chem. Commun.*, 1992, 1668.

12 J-K. F. Buijink, J. H. Teuben, H. Koojman and A. L. Spek, *Organometallics*, 1994, **13**, 2922.

13 See, G. Erker, C. Kruger and G. Muller, *Adv. Organomet. Chem.*, 1985, **24**, 1.