ELSEVIER

Journal of Organometallic Chemistry 487 (1995) C21–C23

Journal of Organometallic Chemistry

Preliminary communication

Synthesis, characterisation and fluxional behaviour of [Ni(η^5-$P_2C_3Bu^t_3$)(η^3-$P_2C_3Bu^t_3$)]

F. Geoffrey N. Cloke *,[a], Kevin R. Flower [a], Cameron Jones [a,1], Robson M. Matos [b], John F. Nixon *,[a]

[a] *School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, UK*
[b] *Departamento de Quimica, ICEx, Universidade Federal de Minas Gerais, Belo Horizonte, MG, CEP: 31270-901, Brazil*

Received 8 June 1994

Abstract

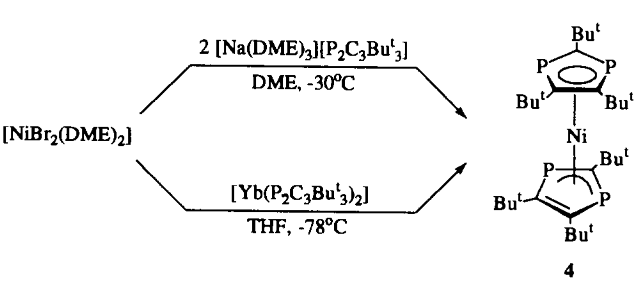
Treatment of either [Na(DME)$_3$][$P_2C_3Bu^t_3$] or [Yb($P_2C_3Bu^t_3$)$_2$] with [$NiBr_2$(DME)$_2$] affords the title compound which displays η^5–η^3-"ring slippage" behaviour in solution.

Keywords: Nickel; Polyphospholyl ligands; Fluxionality; Ring slippage

The chemistry of organo-transition metal systems involving polyphospholyl ligands is of much current interest [1]. We previously reported the first nickel(II) complex, [Ni(η^5-$P_3C_2Bu^t_2$)(η^3-$P_2C_3Bu^t_3$)] **1**, containing both an η^5- and an η^3-bound polypospholyl ligand in the same molecule [2]. More recently, the duality of behaviour of the diphospholyl ring, $P_2C_3Bu^t_3$, has been highlighted in a study which showed that control of the η^5- or η^3-ligating mode could be achieved by the variation of other ligands in the complexes [Mo(η^5-$P_2C_3Bu^t_3$)(η^3-C_9H_7)(CO)$_2$] **2** and [Mo(η^3-$P_2C_3Bu^t_3$)(η^5-C_5Me_5)(CO)$_2$] **3** [3]. We now report that the $P_2C_3Bu^t_3$ ring can act both as an η^5- and an η^3-ligand in the novel bis-disphopholyl nickel complex [Ni(η^5-$P_2C_3Bu^t_3$)(η^3-$P_2C_3Bu^t_3$)] **4**.

Treatment of either [Na(DME)$_3$][$P_2C_3Bu^t_3$] **5** [4] or [Yb($P_2C_3Bu^t_3$)$_2$] **6** [5] with [$NiBr_2$(DME)$_2$] affords **4** (Scheme 1) as a deep blue microcrystalline solid after chromatographic work-up. The formulation of **4** was confirmed by a range of characterisation techniques (microanalysis, MS, ^1H and $^{31}P\{^1H\}$ NMR). Surprisingly, **1** was also obtained as a low yield by-product from the reaction of [$NiBr_2$(DME)$_2$] with **6**. Investigations are currently underway to determine the nature of any ring rearrangement processes occurring during the formation of **1**.

Unlike the well known 20 electron paramagnetic nickelocene, complex **4** gives relatively sharp lines in its ^1H and $^{31}P\{^1H\}$ NMR spectra, suggesting it is an 18 electron diamagnetic system. Its room temperature $^{31}P\{^1H\}$ NMR spectrum exhibits a sharp singlet at 106.4 ppm (Fig. 1(a)) that splits into 4 broad singlets upon cooling to −90°C (Fig. 1(b)). This is exactly the pattern that would be expected for **4** having one η^5- and one η^3-bound ring; it implies that the singlet at room temperature results from an intramolecular dynamic process. The broadness of the low temperature signals can be explained by a lack of resolution of the phosphorus–phosphorus couplings which probably arises from solution viscosity. The ^1H NMR spectrum



4

Scheme 1.

---

* Corresponding authors.

[1] Present address: School of Chemistry, University of Wales, Swansea, Singleton Park, Swansea SA2 8PP, UK.

SSDI 0022-328X(94)05128-3

of **4** at room temperature shows two singlets, in the ratio 1 : 2, which at lower temperatures broaden but display no further splitting, presumably because of overlap of tertiary butyl resonances.

The fluxional behaviour of **4** in solution can be interpreted as involving an η^5--η^3-"ring slippage" of the two $P_2C_3Bu^t_3$ ligands. Such a process can occur via two routes: (i) one involving a 20 electron intermediate in which both rings are η^5-bonded; (ii) one involving a 16 electron intermediate containing two η^3-bound rings.

At present no detailed assignment of the 4 types of ring phosphorus atoms has been made, and we have no evidence to suggest which of these mechanisms is occurring. It seems likely however that the 16 electron intermediate would be the sterically most favourable. It is noteworthy that similar fluxional behaviour was not observed for the closely related complex **1** [2], reflecting the inability of the $P_3C_2Bu^t_2$ ring to bond in an η^3-fashion.

Ring slippage processes of related cyclopentadienyl and indenyl ligands in transition metal complexes are well known phenomena and have been the subject of a recent review [6]. Despite this there are, to the best of our knowledge, only three other examples of complexes containing two identical ligands bonded to the same transition metal in two different ligating modes, without other attendant ligands. The most relevant of these is [Ni(η^5-indenyl)(η^3-indenyl) [7] in which both rings are neither truly η^5- or truly η^3-ligated. In addi-

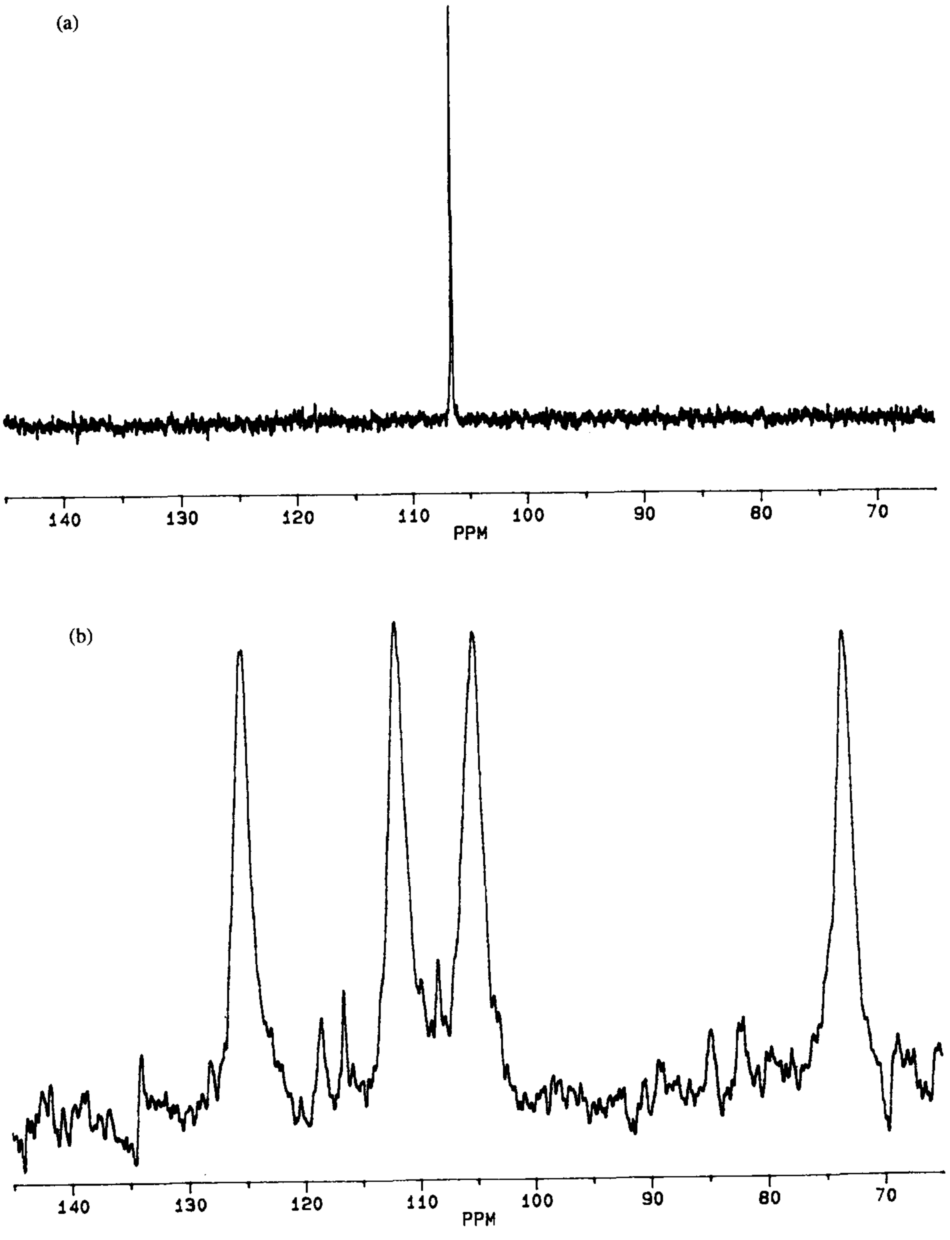


Fig. 1. $^{31}P\{^1H\}$ NMR of [Ni(η^5-$P_2C_3Bu^t_3$)(η^3-$P_2C_3Bu^t_3$)] **4** at (a) 25°C and (b) −90°C.

tion, the bis-arene complexes $[M(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_6)]$ (M = Ru [8], Os [9] have been reported to exhibit a similar fluxionality to **4**, involving a η^6--η^4-"ring slippage" of the two benzene ligands.

The non-formation of a bis-η^5-20 electron complex, $[Ni(\eta^5\text{-}P_2C_3Bu^t_3)_2]$ **7**, in this study is caused either by the resultant steric interactions between its six tertiary butyl groups, or by the presence of higher energy antibonding orbitals in **7** compared with those in its $[M(\eta^5\text{-}C_5H_5)_2]$ analogues. Studies involving use of less sterically demanding disphospholyl ligands than $P_2C_3\text{-}Bu^t_3$ are planned to determine which is the predominant factor.

1. Experimental details

Compound **4**: (a) $[NiBr_2(DME)_2]$ (0.40 g, 1 mmol) was added during 15 min to a solution of $[Na(DME)_3][P_2C_3Bu^t_3]$ (ca. 2 mmol) in DME (15 ml) at −30°C. The suspension was warmed to room temperature and stirred overnight. Volatiles were removed in vacuo to yield a black oil which was purified by column chromatography (kieselgel/hexane) to give **4** as a deep blue powder. 0.42 g, 70%; m.p. 72°C.

(b) $[NiBr_2(DME)_2]$ (0.11 g, 0.28 mmol) was added during 15 min to a solution of $[Yb(P_2C_3Bu^t_3)_2]$ (0.22 g, 0.30 mmol) in THF (25 ml) at −78°C. The suspension was warmed to room temperature and stirred overnight. Volatiles were removed in vacuo to yield a black solid, which was purified by column chromatography (kieselgel/hexane) to give **4**. 40 mg, 25%; $^{31}P\{^1H\}$ NMR (101.256 MHz, toluene-d_8, rel. to 85% H_3PO_4, 25°C) δ: 106.4 (s, 4P); (101.256 MHz, toluene-d_8, rel. to 85% H_3PO_4, −90°C) δ: 119.2, 105.2, 99.6, 67.3 (4 × bs, 4P); ^1H NMR (250 MHz, toluene-d_8, 25°C) δ: 1.57 (s, 18H, $2Bu^t$), 1.51 (s, 36H, $4Bu^t$); mass spectrum (EI): *m/z* 596 (M^+), 458 ($M^+\text{-}C_2Bu^t_2$), 320 ($M^+\text{-}2C_2Bu^t_2$), 169 ($C_2Bu^t_2P$). Found: C 59.53, H 9.03; calc. for $C_{30}H_{54}P_4Ni$: C 60.32, H 9.11.

Acknowledgements

We thank the SERC (CJ, KRF) and CNPq (RMM) for financial support.

References

[1] J.F. Nixon, *Chem. Rev., 88* (1988) 1327, and references therein; *Chem. Ind.*, (1993) 404.

[2] R. Bartsch, P.B. Hitchcock and J.F. Nixon, *J. Organomet. Chem., 373* (1989) C17.

[3] R. Bartsch, P.B. Hitchcock and J.F. Nixon, *J. Chem. Soc., Chem. Commun.*, (1990) 472.

[4] S.S. Al-Juaid, P.B. Hitchcock, R.M. Matos and J.F. Nixon, *J. Chem. Soc., Chem. Commun.*, (1993) 267.

[5] F.G.N. Cloke, K.R. Flower and J.F. Nixon, unpublished results.

[6] J.M. O'Connor and C.P. Casey, *Chem. Rev., 125* (1987) 307.

[7] S.A. Westcott, A.K. Kakkar, G. Stringer, N.S. Taylor and T.B. Marder, *J. Organomet. Chem., 394* (1990) 777.

[8] M.Y. Darensbourg and E.L. Muetterties, *J. Am. Chem. Soc., 100* (1978) 7425.

[9] J.A. Bandy, M.L.H. Green and D. O'Hare, *J. Chem. Soc. Dalton Trans.*, (1986) 2477.