Transition Metal Enolate Chemistry. Formation of a Palladium Alkyl Complex from a Highly Reactive Enolato Palladium Complex

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The ester-derived palladium enolate [LPd{Ph$_2$PCH=C(O)OEt}] **1** (L = o-C$_6$H$_4$CH$_2$NMe$_2$) reacts instantly with dimethyl acetylenedicarboxylate and tetracyanoethylene in tetrahydrofuran (THF) to yield respectively the alkenyl complex [LPd{Ph$_2$PCH[C(O)OEt](MeO$_2$CC=CCO$_2$Me)}] **2** and the alkyl complex [LPd{Ph$_2$PCH[C(O)OEt][(NC)$_2$CC(CN$_2$)]}] **3**.

Whereas the chemistry of enolates associated with alkali metals and early transition metals has been extremely well investigated,[1] the number of studies concerning the reactivity of enolates bound to 'middle' and 'late' transition metals still remains limited. Recent reports about such enolate complexes reveal that these may lead to stereoselective reactions and/or allow convenient functionalizations.[2] Whatever the coordination mode of such enolates is, type **A**, **B** or **C**,[3,4] these compounds preferentially lead with electrophilic species, such as nitriles, isocyanates and alkynes to reactions involving the carbon atom in the position α to the carbonyl group.[5] Palladium enolates have been proposed as intermediates in numerous organic transformations. However, little is known about the steps involved in the reactions of such species. We now describe new aspects of the chemistry of the palladium(II) complex **1**, an oxygen-bound enolate which has previously been reported as being capable of reversible CO$_2$ binding.[6]

Complex **1** reacts almost instantaneously with dimethyl acetylenedicarboxylate in tetrahydrofuran (THF) to yield quantitatively the alkenyl complex **2** [eqn. (1)].† Owing to the

presence in **2** of an asymmetric PCH carbon atom, the two diastereotopic aminomethyl groups appear as distinct signals in the ¹H NMR spectrum [at δ(Me$_a$) 2.71 and δ(Me$_b$) 2.80]. The trans-P-Pd-N stereochemistry is maintained on going from **1** to **2**, as deduced from the $^4J(P-H_3CN)$ values (both 2.6 Hz). The infrared spectrum displays two intense absorption bands at 1715 and 1683 cm⁻¹, corresponding to unco-ordinated ester groups. It is noteworthy that complex **2** contains two trans-bonded carbon atoms, a situation which in view of the high trans influence of the σ-bonded aryl group could lead to further reactivity of the metal–C(alkenyl) bond.

In an effort to generate 'sensitive' palladium–carbon bonds according to reaction (1), we reacted complex **1** with tetracyanoethylene in THF [eqn. (2)]. This reaction leads quantitatively to the alkyl complex **3** which was unambiguously characterized by ¹H, ³¹P, and IR spectroscopy. Although complex **3** is extremely unstable in solution and leads to decomposition, we were able to grow satisfactory crystals for X-ray analysis.‡ The result of this investigation is presented in Fig. 1. The palladium atom which belongs to two five-membered metallacyclic units has a nearly planar coordination environment [max. deviation out of the coordination plane 0.04(1) Å]. The two chelate bite angles are of comparable value [85.4(2)° for P–Pd–C(3) and 82.3(3)° for N(5)–Pd–C(16). The large N(5)–Pd–C(3) angle of 99.1(2)° reflects some steric interaction between the NMe$_2$ group and the two cyano groups connected to C(3). Both chelate rings are puckered especially the phosphorus-containing ring which needs to accommodate three sp³ carbon atoms. The twisting within this metallocycle defines staggered conformations around each of

A   **B**   **C**

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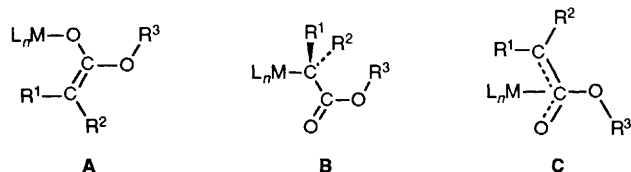
† *Selected spectroscopic data.* For **2**: ν/cm⁻¹ (KBr) 1715s br and 1683s br. ¹H NMR: δ(CDCl$_3$) 0.87 (t, 3 H, CH$_2$CH_3, ^3J 7.2 Hz), 2.71 (d, 3 H, NMe, $^4J_{P,H}$ 2.6 Hz), 2.80 (d, 3 H, NMe, $^4J_{P,H}$ 2.6 Hz), 3.58 (s, 3 H, OMe), 3.74 (s, 3 H, OMe), 4.00 (d, 2 H, NCH$_2$, $^4J_{P,H}$ 1.7 Hz), 4.87 (d, 1 H, PCH, $^2J_{P,H}$ 12.5 Hz) and 6.43–8.16 (14 H, aromatic H). ³¹P{¹H} NMR: δ(THF–C$_6$D$_6$) 60.7 (s).

For **3**: ν/cm⁻¹ (KBr) 2201ms and 1734s. ¹H NMR: δ(CDCl$_3$) 1.06 (t, 3 H, CH$_2$CH_3, ^3J 7.1 Hz), 2.92 (d, 3 H, NMe, $^4J_{P,H}$ 1.3 Hz), 3.16 (d, 3 H, NMe, $^4J_{P,H}$ 3.6 Hz), 3.61 and 4.55 (ABX spin system, 2 H, NCH$_2$, ^2J 13.7, $^4J_{P,H^A}$ 3.6 and $^4J_{P,H^b}$ 0 Hz), 4.07 (dq, 2 H, OCH$_2$, ^3J 7.1 Hz, the origin of the quartet splitting is tentatively assigned to a $^5J_{P,H}$ coupling of 1.5 Hz), 4.32 (d, 1 H, PCH, $^2J_{P,H}$ 10.4 Hz) and 6.49–8.03 (14 H, aromatic H). ³¹P{¹H} NMR: δ(THF–C$_6$D$_6$) 54.6 (s).

MeO₂CC≡CCO₂Me

THF, room temp.
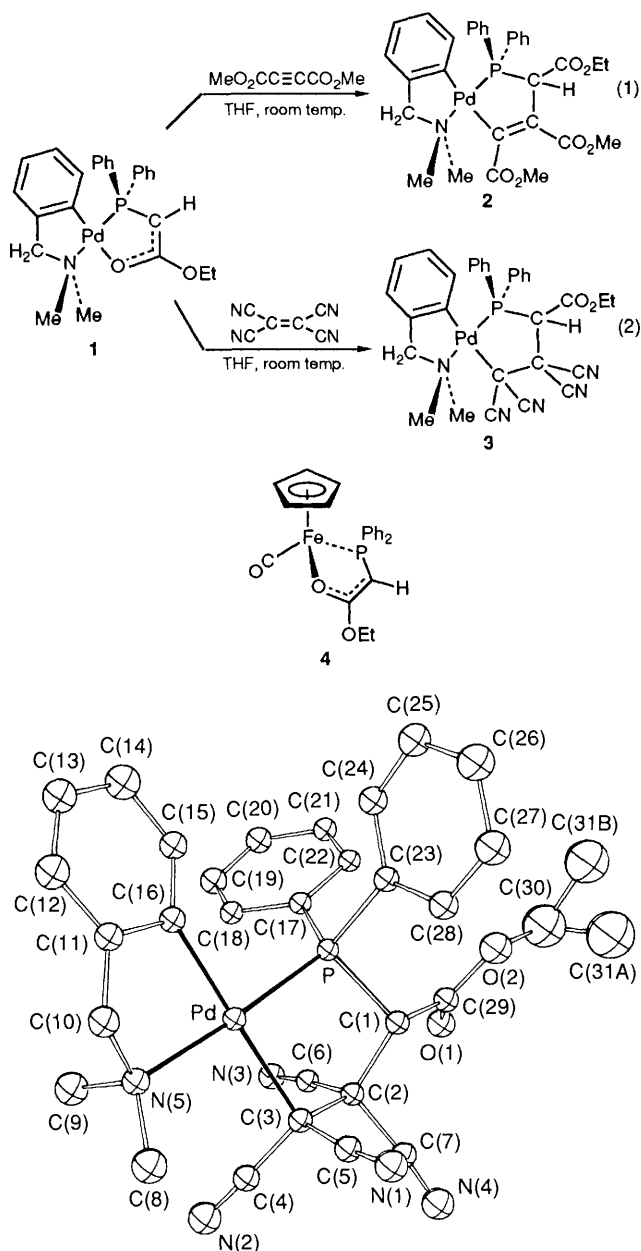
(1)

2

NC⧵C=C⧸CN
NC⧸ ⧵CN

THF, room temp.

(2)

3

4

Fig. 1 Structure of complex 3·0.25 THF: result of the single-crystal structure analysis (solvent molecule not shown). The terminal methyl group is disordered over two positions. Selected bond lengths (Å) and angles (°): Pd–P 2.221(2), Pd–N(5) 215.9(7), Pd–C(3) 221.1(8), Pd–C(16) 202.7(9), P–C(1) 186.6(8), P–C(17) 181.5(7), P–C(23) 182.8(9), C(1)–C(2) 155(1), C(2)–C(3) 158(1), C(1)–C(29) 150(1), O(1)–C(29) 133(1); P–Pd–C(3) 85.4(2), N(5)–Pd–C(16) 82.3(3), P–Pd–C(16) 93.2(3), N(5)–Pd–C(3) 99.1(3), P–C(1)–C(2) 107.9(5), C(1)–C(2)–C(3) 108.0(7), C(2)–C(3)–Pd 110.5(5), C(5)–C(3)–C(2)–C(7) 54.74, C(29)–C(1)–C(2)–C(7) 57.83.

the bonds C(1)–C(2) and C(2)–C(3). The rather high[7] Pd–C(3) bond length [2.211(3) Å] is likely to have its origin in the presence of the four strong electron withdrawing cyano groups and is also consistent with the high *trans* influence of the metallated aryl group. We note that the three other Pd–X bond distances (X = atom of the coordination sphere) fall in the expected normal range.[8] The long Pd–C(3) bond appears to be responsible for the high instability of complex 3. Despite the suspected reactivity of this Pd–C bond, an insertion of a second '(NC)₂CC(CN)₂' unit was not observed when treating 3 with a further equiv. of tetracyanoethylene at room temperature.

We believe that the high reactivity of the palladium–enolate 1 toward electrophilic centres as exemplified by reactions (1)

and (2) arises not only from the intrinsic high nucleophilicity of the α-enolate carbon atom but possibly also from the ability of the 16-electron complex to coordinate the alkene or alkyne prior to reaction. It is noteworthy that for the related iron enolate complex [Fe(η⁵-C₅H₅){Ph₂PCH=C(O)OEt}(CO)] 4§ no reaction is observed either with tetracyanoethylene or with dimethyl acetylenedicarboxylate at room temperature. This suggests that the reaction of the Pd–enolate is a nucleophilic attack on a coordinated alkene or alkyne. These considerations may be helpful in finding new transition metal controlled enolate-functionalisations. To the best of our knowledge, complex 3 constitutes the first isolated metal–alkyl complex obtained by transformation of a transition metal enolate.

References

1 See for example: J. Breimair, M. Wieser, B. Wagner, K. Polborn and W. Beck, *J. Organomet. Chem.*, 1991, **421**, 55; A. S. Galiano-Roth, Y.-J. Kim, J. H. Gilchrist, A. T. Harrison, D. J. Fuller and D. B. Collum, *J. Am. Chem. Soc.*, 1991, **113**, 5053; D. Seebach, *Angew. Chem.*, 1990, **29**, 1363; *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1320 and references cited therein; T. Maetzke and D. Seebach, *Organometallics*, 1990, **9**, 3032; E. B. Tjaden and J. M. Stryker, *J. Am. Chem. Soc.*, 1990, **112**, 6420; L. Douce and D. Matt, *C.R. Acad. Sci. Paris, Ser. II*, 1990, **310**, 721; M. D. Curtis, S. Thanedar and W. M. Butler, *Organometallics*, 1984, **3**, 1855; C. H. Heathcock, *Asymmetric Synthesis*, ed. J. D. Morrison, Academic Press, New York, 1984, vol. 3; J. R. Stille and R. H. Grubbs, *J. Am. Chem. Soc.*, 1983, **105**, 1664; S. Gambarotta, C. Floriani, A. Chiesi-Villa and C. Guastini, *J. Am. Chem. Soc.*, 1983, **105**, 1690; E. J. Moore, A. D. Strauss, J. Armantrout, B. D. Santarsiero, R. H. Grubbs and J. E. Bercaw, *J. Am. Chem. Soc.*, 1983, **105**, 2068; R. P. Planalp and R. A. Andersen, *J. Am. Chem. Soc.*, 1983, **105**, 7774; K. G. Moloy and T. J. Marks, *J. Am. Chem. Soc.*, 1983, **105**, 5696; D. A. Evans and L. R. McGee, *Tetrahedron Lett.*, 1980, **21**, 3975; Y. Yamamoto and K. Maruyama, *Tetrahedron Lett.*, 1980, **21**, 4607; M. Manriquez, D. R. Alister, R. D. Sanner and J. E. Bercaw, *J. Am. Chem. Soc.*, 1973, **98**, 6733.

2 J. G. Stack, J. J. Doney, R. G. Bergman and C. H. Heathcock, *Organometallics*, 1990, **9**, 453; B. Guilbert, B. Demerseman, P. H. Dixneuf and C. Mealli, *J. Chem. Soc., Chem. Commun.*, 1989, 1035; S.-E. Bouaoud, P. Braunstein, D. Grandjean, D. Matt and D. Nobel, *Inorg. Chem.*, 1988, **27**, 2279.

3 For some *C*- or *O*-bound enolates see: E. R. Burkhardt, J. M. Stack, C. H. Heathcock and R. G. Bergman, *Pure Appl. Chem.*, 1988, **60**, 1; S.-E. Bouaoud, P. Braunstein, D. Grandjean, D. Matt and D. Nobel, *J. Chem. Soc., Chem. Commun.*, 1987, 488; N. Yanase, Y. Nakamura and S. Kawaguchi, *Inorg. Chem.*, 1980, **19**, 1575; H. D. Empsall, S. Johnson and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1980, 302.

4 For some examples of η³-oxallyl structures see for example: Y. Ito, T. Hirao and T. Saegusa, *J. Org. Chem.*, 1978, **43**, 1011; R. W. Goetz and M. Orchin, *J. Am. Chem. Soc.*, 1963, **85**, 278.

5 E. R. Burkhardt, R. G. Bergman and C. H. Heathcock, *Organometallics*, 1990, **9**, 30.

6 P. Braunstein, D. Matt and D. Nobel, *Chem. Rev.*, 1988, **88**, 747.

7 The calculated sum of the covalent radii of palladium(II) and carbon of hybridization sp³ is 2.07 Å. See: G. Wilkinson, F. G. A. Stone and E. W. Abel, *Comprehensive Organometallic Chemistry*, Pergamon, Oxford, 1982, vol. 6, p. 408.

8 P. Braunstein, D. Matt, D. Nobel, S.-E. Bouaoud and D. Grandjean, *J. Organomet. Chem.*, 1986, **301**, 401.

§ Complex **4** was prepared using the following procedure: a THF solution (20 ml) of [Fe(η⁵-C₅H₅)I(CO){Ph₂PCH₂C(O)OEt}] (1.000 g, 1.82 mmol) was stirred for 15 h with NaH (0.048 g, 2.000 mmol). The solution was concentrated to *ca.* 50% and filtered through a glass frit. Addition of pentane afforded dark brown crystals of **4** (0.560 g, 73%). Satisfactory elemental (C,H) analysis was obtained. IR (KBr) v/cm⁻¹: 1951s (CO) and 1508s (C–O and C=C). IR (THF) v/cm⁻¹ 1956s (CO) 1511m and 1506sh (C–O and C=C). ¹H NMR (C₆D₆) δ 1.06 (t, 3 H, Me, ³*J* 7.0 Hz), 3.94 (s, 1 H, PCH, ²*J*ₚ,ₕ 0 Hz), 3.95 (q, 2 H, CH₂, ³*J* 7.0 Hz), 4.10 (s, 5 H, η⁵-C₅H₅) and 7.03–7.66 (10 H, aromatic H). ³¹P{¹H} NMR (THF–C₆D₆) δ 58.8 (s).