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Reactivity of an anionic Pd(II) metallacycle with CH_2X_2 (X = Cl, Br, I): formal insertion of methylene into a Pd–C_{aryl} bond†

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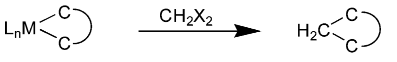
Whereas the reaction of the anionic palladium metallacycle $[\mathrm{K}\{\overline{\mathrm{Pd}(\mathrm{CH_2CMe_2}\text{-}o\text{-}\mathrm{C}}{}_6\mathrm{H_4})(\kappa^2\text{-Tp})\}]$ with CH_2Cl_2 leads to the isolation of the stable Pd(IV) chloromethyl complex $[\overline{\mathrm{Pd}(\mathrm{CH_2CMe_2}\text{-}o\text{-}\mathrm{C}}{}_6\mathrm{H_4})(\kappa^3\text{-Tp})(\mathrm{CH_2Cl})]$, the analogous reactions with CH_2Br_2 and CH_2I_2 give rise to the six membered metallacycles $[\overline{\mathrm{Pd}(\mathrm{CH_2CMe_2}\text{-}o\text{-}\mathrm{C_6H_4}(\mathrm{CH_2}}))(\kappa^3\text{-Tp})\mathrm{X}]$ (X = Br or I), as a result of the formal insertion of CH_2 into the Pd–C_{aryl} bond.

The formation of C–C bonds mediated by palladium is an extremely useful and widespread tool in organic synthesis.[1] As an example, treatment of palladium metallacycles with dihalomethanes often results in the formation of carbocycles, by a double C–C coupling reaction (eqn. (1)). This process has additional interest as a characterization method for metallacyclic complexes of Pd and other elements, as the final products are easily detected and identified.[2] However, little is known of the intimate mechanism of this seemingly simple reaction, since intermediate species are usually too unstable to be detected.[3] Herein we report the isolation and characterization of intermediate products of the reaction of Pd(II) metallacycles with dihalomethanes.



(1)

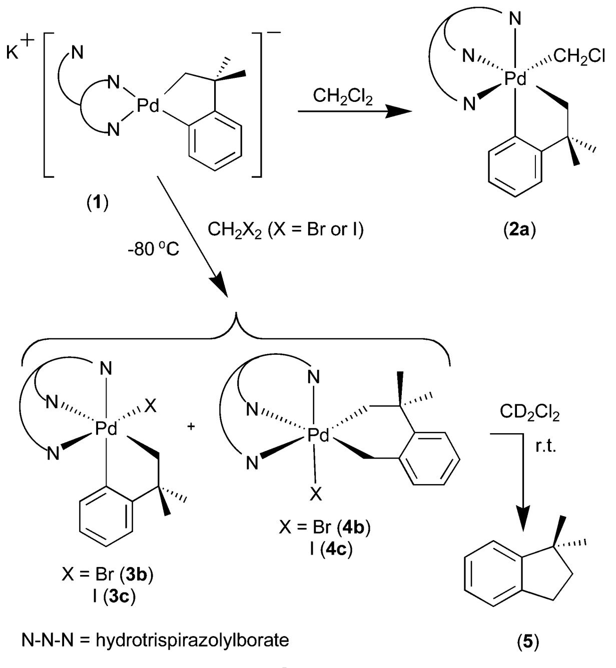
Anionic organopalladium compounds containing rigid tripodal ligands (*e.g.* Tp) undergo oxidative addition reactions with alkyl halides, giving rise to stable Pd(IV) complexes.[4] We have recently shown that the readily prepared Pd(II) metallacycle $[\mathrm{K}\{\overline{\mathrm{Pd}(\mathrm{CH_2CMe_2}\text{-}o\text{-}\mathrm{C}}{}_6\mathrm{H_4})(\kappa^2\text{-Tp})\}]$ (**1**) constitutes an excellent starting material for the synthesis of different types of Pd(IV) complexes.[5] Continuing these studies, we have examined the reaction of **1** with different dihalomethanes, and characterized the products thereof.

Compound **1** reacts slowly with CH_2Cl_2. In dichloromethane solution, full conversion into the chloromethyl derivative $[\overline{\mathrm{Pd}(\mathrm{CH_2CMe_2}\text{-}o\text{-}\mathrm{C}}{}_6\mathrm{H_4})(\kappa^3\text{-Tp})(\mathrm{CH_2Cl})]$ **2a** requires *ca.* 36 h at room temperature (Scheme 1). In comparison with other Pd(IV) complexes, **2a** shows high thermal stability, and can be heated up to 90 °C without apparent decomposition.

Spectroscopic data for **2a** are consistent with the structure proposed in Scheme 1. The ^{1}H NMR spectrum displays resonances due to two AX spin systems at δ 3.65 and 4.17 ppm ($^2J_{HH}$ = 7.9 Hz) and 4.60 and 4.68 ($^2J_{HH}$ = 5.9 Hz), assigned to two methylene groups with the aid of 2-D ^{1}H-^{1}H COSY and ^{1}H-^{13}C HMQC correlation spectra. In the long range ^{1}H-^{13}C HMBC heterocorrelation spectrum, the signals corresponding to the former methylene group are connected with the resonances of the CMe_2 unit and therefore can be assigned to the endocyclic CH_2, while those of the latter show no correspondences with other resonances, as expected for a Pd-bound CH_2Cl group.

The analogous reactions of **1** with 10 equiv. of CH_2Br_2 or CH_2I_2 in acetone are very fast even at low temperatures (−78 °C). Analysis of the reaction mixtures by ^{1}H NMR reveals the formation of two main products (**3b,c** and **4b,c**, respectively, combined isolated yield *ca.* 50–60%), together with minor amounts of other Pd(IV) species. The precise ratio in which compounds **3** and **4** are formed depends upon the experimental conditions, but **4** is always the major product, and **4** : **3** ratios as large as 10 : 1 have been achieved for X = I. The separation of these products poses important experimental difficulties, due to their tendency to co-crystallize. However, workup involving a preliminary chromatographic purification of the **3**/**4** mixture, followed by repeated washing with Et_2O (a solvent in which complexes **3** are slightly more soluble) allowed the isolation of analytically pure samples of **4b** and **4c**. In CD_2Cl_2 solution at room temperature, compounds **4b** and **4c** slowly undergo reductive elimination, giving 1,1-dimethylindan, **5**, in quantitative spectroscopic yield, together with unidentified Pd products.

Compounds **3** can be readily identified as the halogenation products of **1**, $[\overline{\mathrm{Pd}(\mathrm{CH_2CMe_2}\text{-}o\text{-}\mathrm{C}}{}_6\mathrm{H_4})(\kappa^3\text{-Tp})\mathrm{X}]$ (X = Br, **3b**; I, **3c**), by comparison of their NMR spectra with those of samples prepared independently.[6] The NMR spectra of **4b** and **4c** are very similar. Like **2a**, their ^{1}H NMR spectra display two sets of AX doublets attributable to two CH_2 groups. However, the distribution of the methylene signals in **4b/c** differ from that observed for **2a**, suggesting that their structures could be different.‡ Thus, cross-peaks are found in the ^{1}H-^{13}C HMBC spectra of **4b** and **4c**, that connect the resonances of the two CH_2 groups with those of the $-CMe_2$-*o*-C_6H_4- fragment. For instance, in **4c** the ^{1}H resonances of



Scheme 1

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† Electronic supplementary information (ESI) available: full experimental and characterization data and crystallographic information (CIF format). See http://www.rsc.org/suppdata/cc/b4/b403411b/

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one of the two CH_2 groups (δ 3.60, 4.92) are connected to the ^{13}C signals of the CMe_2 unit, while the proton signals of the other CH_2 group (δ 3.71, 6.42) correlate with one of the aromatic ^{13}C resonances. The latter correspondence indicates that the second CH_2 has become part of the metallacycle, as a result of its formal insertion into the Pd–C_{aryl} bond. Confirmation of this proposal comes from the X-ray structure of **4b** (Fig. 1).§ As anticipated, the geometry of the metal centre is essentially octahedral, with tridentate facial coordination of the Tp ligand. The two Pd–C bonds have similar lengths, 2.049(8) and 2.062(7) Å for Pd–C(1) and Pd–C(11) respectively.

^1H NMR monitoring of the reaction of **1** with CH_2Br_2 in acetone-d_6 allows the detection of an intermediate species, **2b**, characterized by two sets of diastereotopic CH_2 resonances. The chemical shifts and coupling constants of these signals (δ 3.65, 4.15, $^2J_{HH}$ = 7.6 Hz and δ 4.36, 4.43, $^2J_{HH}$ = 5.6 Hz) are very similar to those found for **2a**, indicating that the two compounds have similar structures. Therefore, halomethyl complexes **2b** and **2c** are likely intermediates *en route* to the six membered metallacycles **4** (Scheme 2), although **2c** is too unstable to allow detection.

The formation of significant amounts of complexes **3** suggests that the S_N2 mechanism that usually operates in oxidative addition reactions to Pd(II) is competitive with a free radical process in the case of the very reactive dihalometanes CH_2Br_2 and CH_2I_2. However, the most interesting aspect of this process concerns the mechanism of the CH_2 migration. A likely route (A, Scheme 2) involves a reductive coupling of the CH_2X and the aryl group, to afford a Pd(II) complex that subsequently experiences an intramolecular oxidative addition of the CH_2–X bond. The relative stability of the intermediates **2** suggests that the ability to undergo the CH_2 migration process increases in the order $CH_2Cl < CH_2Br < CH_2I$. This matches the trend in the strength of the Pd–CH_2X bonds that can be anticipated considering the group electronegativity and size of the halomethyl ligand.[7] The preference for alkyl–aryl coupling is substantiated by previous studies on the selectivity of Pd(IV) reductive elimination reactions.[8]

Notwithstanding the above, an attractive alternative mechanistic pathway involving a transient Pd(IV) carbene complex (route B) is conceivable as well. Interestingly, the observed reactivity trend fits well with the facility of the halide dissociation from the Pd–CH_2X linkage (I > Br > Cl). Carbene insertion reactions in isoelectronic Ir(III) complexes have been observed before.[9] Further studies to decide between mechanistic pathways A and B are currently in progress in our laboratories.

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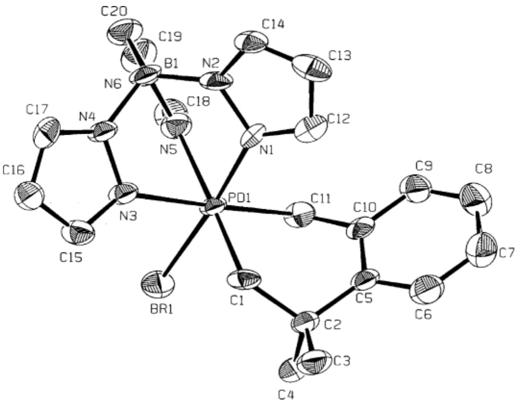
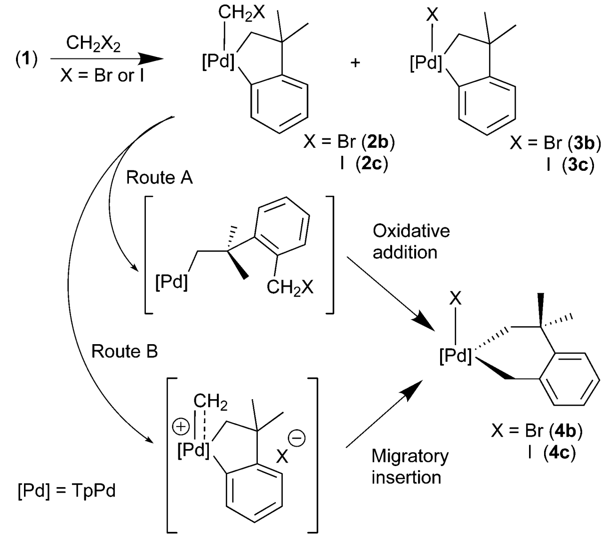


Fig. 1 ORTEP diagram of complex **4b**.



Scheme 2

Notes and references

‡ Selected ^1H NMR data for **4b** and **4c** (CD_2Cl_2, 20 °C): **4b**: δ 3.79, 4.75 (AX system, $^2J_{HH}$ = 7.1 Hz, CH_2–CMe_2); δ 4.07, 6.33 (AX system, $^2J_{HH}$ = 8.6 Hz, CH_2–Ar). **4c**: δ 3.60, 4.92 (AX system, $^2J_{HH}$ = 7.4 Hz, CH_2–CMe_2); δ 3.71, 6.42 (AX system, $^2J_{HH}$ = 8.7 Hz, CH_2–Ar) The strong deshielding of one of the CH_2 protons may be due to its proximity to the aromatic pyrazolyl rings.

§ Crystal data for **4b**: $C_{20}H_{24}BBrN_6Pd$, M = 545.56, triclinic, $P\bar{1}$, a = 10.307(3), b = 11.881(3), c = 10.056(3) Å, α = 107.20(2)°, β = 115.02(2)°, γ = 75.17(2)°, U = 1053.8(6) Å^3, Z = 2, D_c = 1.719 g cm^{-3}, λ = 0.71073 Å, T = 290 K. total reflections = 3714, unique reflections = 3714 (R_{int} = 20.340). Final R = 0.0568, Rw = 0.0671 (all data). *GoF* = 2.957. CCDC 233562. See http://www.rsc.org/suppdata/cc/b4/b403411b/ for crystallographic data in .cif or other electronic format

1 J. Tsuji, *Palladium Reagents and Catalyst*, John Wiley & Sons Ltd, Chichester, 1995.
2 J. Cámpora, P. Palma and E. Carmona, *Coord. Chem. Rev.*, 1999, **195**, 207and references herein.
3 Although no intermediates seem to have been isolated in these reactions, there are many reports of C–X oxidative addition of dihalomethanes. See for example: (*a*) G. E. Ball, W. R. Cullen, M. D. Fryzuk, B. R. James and S. J. Rettig, *J. Chem. Soc., Dalton Trans.*, 1991, 3767; (*b*) A. L. Balch, C. T. Hunt, C.-L. Lee, M. M. Olmstead and P. J. James, *J. Am. Chem. Soc.*, 1981, **103**, 4764.
4 See for instance: (*a*) A. J. Canty, H. Jin, A. S. Roberts, B. W. Skelton and P. R. Traill, *Organometallics*, 1995, **14**, 199; (*b*) A. J. Canty, J. L. Hoare, N. W. Davies and P. R. Traill, *Organometallics*, 1998, **17**, 2046.
5 J. Cámpora, D. del Río, E. Carmona, P. Palma, C. Graiff and A. Tiripicchio, *Organometallics*, 2003, **22**, 3345.
6 Compounds **3b** and **3c** can be readily prepared by direct halogenation of **1** with NBS or I_2.
7 J. P. Collman, L. S. Hegedus, J. R. Norton and R. G. Finke, *Principles and Applications of Organotransition Metal Chemistry,* University Science books, Mill Valley, CA, 1987.
8 See for instance: (*a*) M. Catellani, G. Bocelli and S. Ghelli, *J. Organomet. Chem.*, 1993, **458**, C12; (*b*) B. A. Markies, A. J. Canty, M. D. Janssen, A. L. Speck, J. Boersma and G. van Koten, *Recl. Trav. Chim. Pays-Bas*, 1991, **110**, 477.
9 F. M. Alías, M. L. Poveda, M. Sellin and E. Carmona, *J. Am. Chem. Soc.*, 1998, **23**, 5816.