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Preliminary communication

Studies of oxidative addition-reductive elimination reactions, and the crystal structure of the palladium(IV) complex $Me_2(p\text{-}BrC_6H_4CH_2)Pd(phen)Br$

Allan J. Canty, Andrew A. Watson,

Chemistry Department, University of Tasmania, Hobart, Tasmania 7001 (Australia)

Brian W. Skelton and Allan H. White

Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands, W.A. 6009 (Australia)

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Abstract

Selectivity in reductive elimination of ethane and RMe has been observed for benzyl and phenacyl complexes $Me_2RPd(L_2)Br$ (L_2 = bipy, phen), with product ratios dependent upon R and L_2, and cationic intermediates detected by ^1H NMR spectroscopy for oxidative addition of CD_3I and phenacyl bromides to $Me_2Pd(L_2)$. The crystal structure of *fac*-$Me_2(p\text{-}BrC_6H_4CH_2)Pd(phen)Br$ has been determined.

Oxidative addition and reductive elimination reactions are of fundamental importance in organometallic chemistry and catalysis, and the recent development of hydrocarbylpalladium(IV) chemistry provides a new system for the study of such reactions under mild conditions [1]. The reagents $p\text{-}XC_6H_4CH_2Br$ (X = H, Br, NO_2) and $p\text{-}XC_6H_4COCH_2Br$ (X = H, Br) react with the 2,2′-bipyridyl and 1,10-phenanthroline complexes, $Me_2Pd(L_2)$, in acetone at 0 °C to form $Me_2RPd(L_2)Br$ (satisfactory C, H, N analyses). Crystals of $Me_2(p\text{-}BrC_6H_4CH_2)Pd(phen)Br$, $C_{21}H_{20}Br_2N_2Pd$, are monoclinic *, $M = 566.6$, space group $P2_1/n$, with a 8.465(2), b 9.051(2), c 26.364(6) Å, β 96.75(2)°, $Z = 4$. 2399 'observed', absorption-corrected diffractometer reflections to $2\theta_{max}$ 50° (Mo-K_α radiation) were refined by full-matrix least squares to $R = 0.034$. The benzyl group is *trans* to the bromine atom (Fig.

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* The atomic coordinates, bond lengths and angles, and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW (Great Britain). Any request for them should be accompanied by a full literature citation for this communication.

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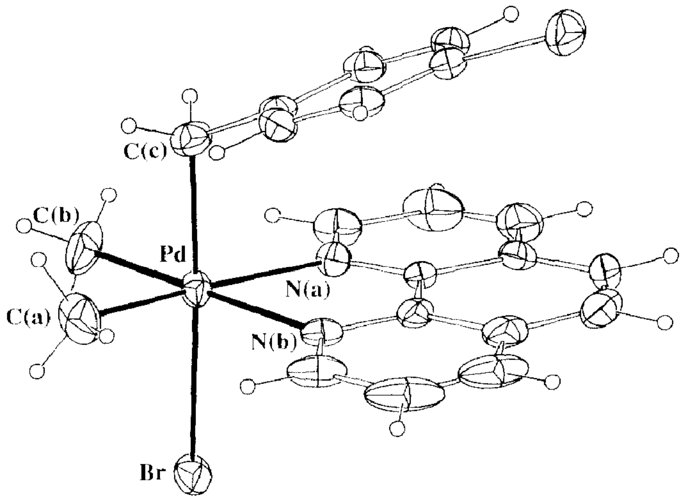

Fig. 1. A molecular projection for *fac*-[Me_2(*p*-$BrC_6H_4CH_2$)Pd(phen)Br] showing selected atom numbering; 20% thermal ellipsoids are shown for the non-hydrogen atoms, and hydrogen atoms (constrained at estimated idealized positions) have been given an arbitrary radius of 0.1 Å. Selected bond distances and angles: Pd–C(a,b,c) 2.033(7), 2.033(7), 2.091(6) Å, Pd–N(a,b) 2.191(4), 2.198(5) Å, Pd–Br 2.636(1) Å, C(a)–Pd–C(b,c) 85.1(3), 89.2(3)°, C(b)–Pd–C(c) 84.6(3)°, C(a)–Pd–N(a,b) 173.2(3), 97.2(3)°, C(b)–Pd–N(a,b) 101.6(2), 177.6(2)°, C(c)–Pd–N(a,b) 90.2(2), 95.8(2)°, Br–Pd–C(a,b,c) 91.9(2), 90.4(2), 174.8(2)°, Br–Pd–N(a,b) 89.3(1), 89.2(1)°, N(a)–Pd–N(b) 76.1(2)°.

1), and the Pd–CH_2 bond length is 2.091(6) Å, ca. 0.03 Å longer than that of Pd–CH_3 in the same complex, and in the only two organopalladium(IV) complexes examined crystallographically [1,2], both containing the simple *fac*-Me_3Pd unit. The Pd–Br bond length, 2.636(1) Å, appears to be the determination of a Pd^{IV}–Br bond length [3,13].

Selectivity in reductive elimination reactions from $R_2R'Pd^{IV}$ centres occurs in some catalytic reactions, e.g. in the synthesis of hexahydromethanotriphenylenes [4], and although the large majority of coupling reactions employing palladium catalysts involve Pd^0–Pd^{II} cycles [5], Pd^{IV} intermediates have been implicated in some processes, e.g. in methyl–methyl and methyl–benzyl coupling [6]. Slow warming of the complexes $Me_2RPd(L_2)Br$ in $(CD_3)_2CO$ to 40 °C cleanly generates $RPd(L_2)Br$ + MeMe, and $MePd(L_2)Br$ + RMe, although the high selectivity for ethane evolution in most reactions and the complexity of some spectra rendered detection of RMe uncertain in some cases. The product distribution depends on both R and L_2, with Me_2(*p*-$XC_6H_4CH_2$)Pd(bipy)Br (X = H, Br, NO_2) giving exclusively RPd(bipy)Br + MeMe [7*,9*], Me_2(*p*-$XC_6H_4CH_2$)Pd(phen)Br giving RPd(phen)Br and MePd(phen)Br in ca. 3/1 ratio, Me_2(*p*-$BrC_6H_4COCH_2$)Pd(L_2)Br giving $RPd(L_2)Br$ and $MePd(L_2)Br$ in ca. 5/1 ratio (bipy) and ca. 2/1 ratio (phen), and $Me_2(C_6H_5COCH_2)Pd(L_2)Br$ giving $RPd(L_2)Br$ and $MePd(L_2)Br$ in ca. 3/1 ratio (bipy) and ca. 1/1 ratio (phen) [10*]. The reactions strongly favour ethane elimination, more so with the bipy than the phen complexes, since a random loss of MeMe and RMe would give a 1/2 ratio for $RPd(L_2)Br/MePd(L_2)Br$.

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* Reference numbers with asterisks indicate notes in the list of references.

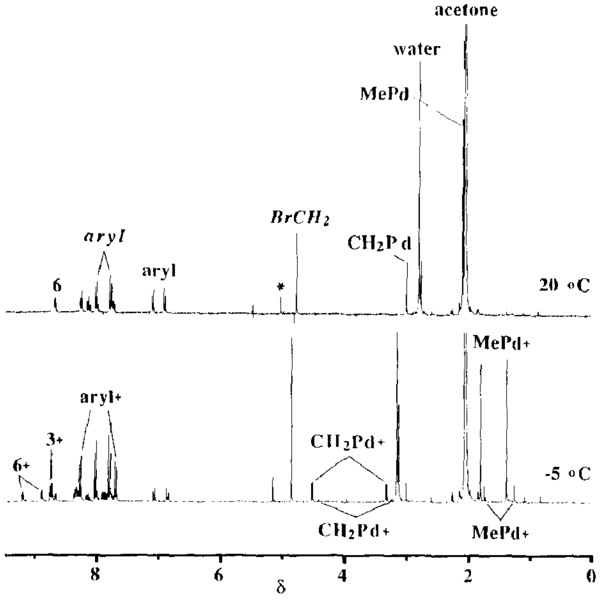

Fig. 2. ^{1}H NMR spectra obtained on addition of an excess of p-$BrC_6H_4COCH_2Br$ to $Me_2Pd(bipy)$ in $(CD_3)_2CO$ at −5 °C, followed by warming to 20 °C, showing selected assignments, with peaks for the unchanged reagent in italics. The major cationic intermediate clearly shows two H(6)(bipy), MePd, and CH_2 resonances. The peaks for them are marked, minor cation is below the spectrum at −5 °C. The stable neutral product (20 °C) has the MePd resonance close to acetone, but this resonance is clearly identified in $CDCl_3$ for the isolated complex. *Indicates an impurity.

Spectroscopic detection of cationic intermediates in S_N2 oxidative additions appears to be limited to Me_2Pt^{II} systems [11]. In studies at −5 °C with $Me_2Pd(bipy)$ and the phenacyl bromides, the ^{1}H NMR spectra (e.g. Fig. 2) show the stable neutral product as a minor species, together with two intermediates, one in trace amount, and both intermediates (assumed "*fac*-C_3Pd" octahedral) have the phenacyl group *trans* to a bipy nitrogen. They have MePd resonances upfield from the neutral product, as expected for cations [12*], and on warming to ca. 20 °C only the stable product with the phenacyl group *trans* to bromine is observed, and the spectrum is unaltered on recooling. Kinetic studies indicate that MeI and $PhCH_2Br$ react with $Me_2M(L_2)$ (M = Pd, Pt) by the S_N2 mechanism [8], and we have now found that at −50 °C CD_3I forms an intermediate cation $[Me_2(CD_3)Pd(ibpy)((CD_3)_2CO)]^+$ [12*], with spectra similar to that reported for the Pt^{IV} cation [11], except that the Me and CD_3 groups are scrambled, reflecting more rapid isomerization for palladium. The S_N2 mechanism is expected to give R (or CD_3) *trans* to $(CD_3)_2CO$ and *cis* to bipy, as observed for platinum [11], and thus for more labile palladium, the major intermediate observed on oxidative addition of phenacyl bromides to $Me_2Pd(bipy)$, with R *trans* to bipy, is assumed to be the most stable isomer for the cation. The major cation may be stabilized by intramolecular coordination of the carbonyl group, $[Me_2(R\text{-}C,O)Pd(bipy)]^+$, rather than $(CD_3)_2CO$ coordination, $[Me_2RPd(bipy)((CD_3)_2CO)]^+$, since oxidative addition of the benzyl bromides show only traces of one cation (benzyl *cis* to bipy) at low temperature.

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References and notes

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3 See, e.g. L.R. Gray, D.J. Gulliver, W. Levason, and M. Webster, J. Chem. Soc., Dalton Trans., (1983) 133.

4 M. Catellani and G.P. Chiusoli, J. Organomet. Chem., 346 (1988) C27.

5 See, e.g. J.M. Brown and N.A. Cooley, J. Chem. Soc., Chem. Commun., (1988) 1345, and ref. therein.

6 D. Milstein and J.K. Stille, J. Am. Chem. Soc., 101 (1979) 4981, 4992; A. Gillie and J.K. Stille, ibid., 102 (1980) 4933; A. Moravskiy and J.K. Stille, ibid., 103 (1981) 4182.

7 With the extreme and less comparable approach of heating solid samples of $Me_2(PhCH_2)Pd(L_2)Br$ to the decomposition temperatures of ca. 145 °C (bipy) and 120 °C (phen), a less pronounced preference for ethane evolution is found [8].

8 K.-T. Aye, A.J. Canty, M. Crespo, R.J. Puddephatt, J.D. Scott, and A.A. Watson, Organometallics, in press.

9 The unstable complex $Me_2(PhCH_2)Pd(tmeda)Br$, detected at low temperature by NMR spectroscopy, also loses ethane exclusively (W. de Graaf, J. Boersma, D. Grove, A.L. Spek, and G. van Koten, Rec. Trav. Chim. Pays-Bas, 107 (1988) 299).

10 These two complexes also give a small amount of MeBr (2.70 ppm, partially removed by later purging with N_2 for ca. 30 sec), together with a transient resonance at 0.47 (bipy) and 0.61 ppm (phen). These resonances are assigned to unstable $Me(C_6H_5COCH_2)Pd(L_2)Br$ since the MePd resonance of the bipy complex occurs 0.14 ppm upfield from the phen complex, exactly as found for $Me_2Pd(L_2)$.

11 M. Crespo and R.J. Puddephatt, Organometallics, 6 (1987) 2548, and ref. therein.

12 $[Me_3Pd(bipy)((CD_3)_2CO)]^+$ has δ(MePd) at 1.61 and 0.82 ppm (2/1 ratio), upfield from $Me_3Pd(bipy)I$ (1.77 and 1.11 ppm (2/1 ratio)) at −50 °C, but is completely converted into the latter on warming to ca. 0 °C.

13 *Note added in proof*: $[(CH_2NH_3)_2][PdBr_6]$ has Pd–Br 2.466(3) and 2.470(3) Å (R.J.H. Clark, V.B. Croud, H.M. Dawes and M.B. Hursthouse, Polyhedron, 24 (1988) 2611).