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Organopalladium(IV) Chemistry: Binuclear Pd^{IV}–Pd^{IV} and Pd^{IV}–Pt^{IV} μ-Hydrocarbyl Complexes

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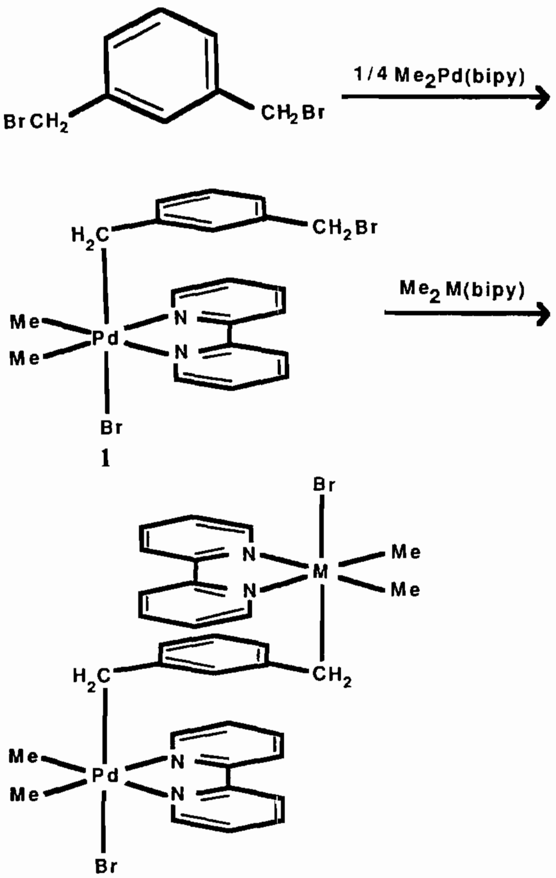
Alkylpalladium(IV) chemistry has developed rapidly [1–7] since the initial synthesis of the 2,2′-bipyridyl complex *fac*-$Me_3Pd(bipy)I$ in 1986 [1], including: reports of kinetic studies of the *trans*-oxidative addition of iodomethane to $Me_2Pd(bipy)$ to form *fac*-$Me_3Pd(bipy)I$ and subsequent reductive elimination of ethane to form *cis*-$MePd(bipy)I$ [5]; an estimation of the Pd–C bond energy for *fac*-$Me_3Pd(bipy)I$ [5]; isolation of cationic complexes [2–4], e.g. [*fac*-Me_3Pd{tris(pyrazol-1-yl)methane}]I [2]; detection of cations for bidentate ligands in solution, e.g. [*fac*-$Me_3Pd(bipy)(NCMe)]^+$ [5]; and detection of complexes at low temperature by NMR spectroscopy [3, 4, 6, 7], e.g. *trans*-oxidative addition of allyl bromide to form *fac*-$Me_2(CH_2{=}CH\text{-}CH_2)Pd(bipy)Br$ [4] and *cis*-oxidative addition of benzyl bromide to form *fac*-$Me_2(PhCH_2)Pd$(tetramethylethylenediamine)Br [6].

It has become apparent that, with the appropriate choice of alkyl groups and ligands, alkylpalladium(IV) complexes of considerable stability in both the solid state and solution are accessible [4]. There is considerable current interest in μ-hydrocarbyl transition metal complexes [8] and, noting that facile *trans*-oxidative addition of benzyl bromide to $Me_2Pd(bipy)$ gives ambient temperature stable *fac*-$Me_2(PhCH_2)Pd(bipy)Br$ [4], we have attempted oxidative addition reactions with α,α'-*meta*-dibromoxylene, resulting in isolation of the first examples of (μ-hydrocarbyl)dipalladium(IV) and (μ-hydrocarbyl)-palladium(IV)platinum(IV) complexes (Scheme 1).



2: M = Pd
3: M = Pt

Scheme 1.

Reaction of *m*-$(BrCH_2)_2C_6H_4$ with $Me_2Pd(bipy)$ in a 4:1 molar ratio (organohalide in excess to minimise formation of 2) in acetone at 0 °C gave a small quantity of a white precipitate, identified as a mixture of 1 and 2, and addition of hexane to the filtrate gave the complex 1 in *ca.* 32% yield. Complex 1 dissolves in $CDCl_3$ to give a simple ^1H NMR spectrum showing resonances and integration as expected for *trans*-oxidative addition to form *fac*-Me_2(*m*-$(CH_2Br)C_6H_4CH_2)Pd(bipy)Br$; e.g. benzene ring resonances at 6.77 (1H), 6.62 (1H) and 6.41 (2H) ppm, CH_2Br at 4.13 ppm, and with CH_2Pd and Me_2Pd at 3.16 and 2.03 ppm, similar to the values reported [4] for the related complex *fac*-$Me_2(PhCH_2)Pd(bipy)Br$ of 3.17 and 1.98 ppm.

The binuclear complexes 2 and 3 were obtained on oxidative addition of the 'organohalide' 1 to $Me_2M(bipy)$ in chloroform/acetone with subsequent addition of hexane; synthesis of the dipalladium complex $\{Me_2Pd(bipy)Br\}_2(\mu\text{-}m\text{-}(CH_2)_2C_6H_4)$ (2) directly from *m*-$(BrCH_2)_2C_6H_4$ and $Me_2Pd(bipy)$ in a 1:2 ratio in acetone is preferred, since this procedure gives a higher yield (*ca.* 70%), and the synthesis from 1 requires the presence of chloroform to dissolve 1, although $Me_2Pd(bipy)$ is sensitive to chloroform. The binuclear complexes have satisfactory microanalyses (C, H, N) and similar infrared spectra which differ from the spectrum of 1, and although the palladium(IV) complexes slowly decompose at ambient temperature they may be satisfactorily stored at *ca.* −20 °C.

The binuclear complexes are insufficiently soluble in $CDCl_3$ or $(CD_3)_2CO$ for ^1H NMR spectroscopy,

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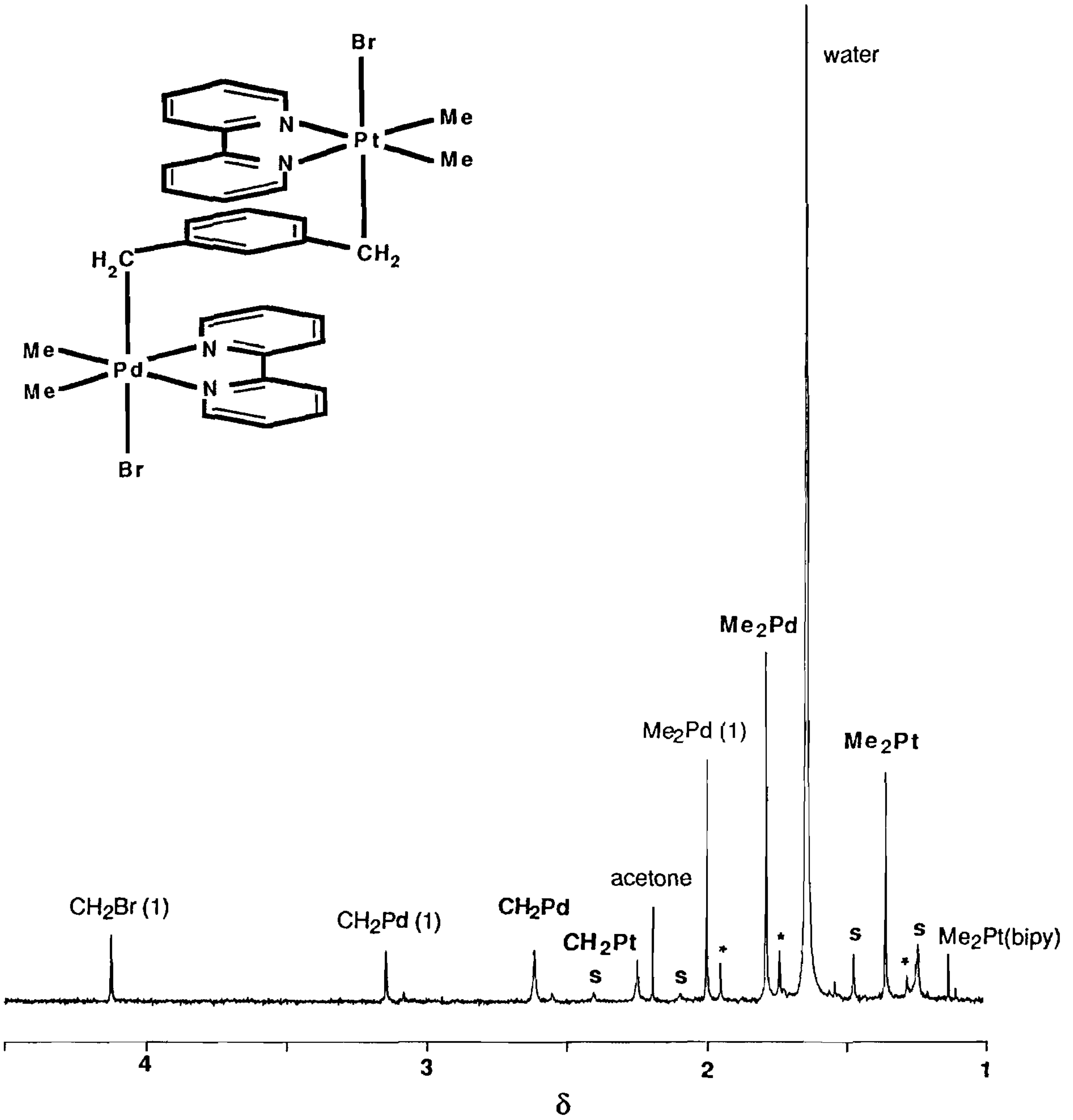

Fig. 1. The ^{1}H NMR spectrum in the upfield region obtained on oxidative addition of Me_2(*m*-(CH_2Br)$C_6H_4CH_2$)Pd(bipy)Br (1) to Me_2Pt(bipy) in $CDCl_3$ at 0 °C, 4 min after mixing and prior to completion of reaction, showing the presence of Me_2Pd(bipy)-Br(μ-*m*-(CH_2)$_2C_6H_4$)Me_2Pt(bipy)Br (3) (assignments for **3** in bold type, s indicates $^2J(^1H-^{195}Pt)$ satellites), together with unreacted **1**, Me_2Pt(bipy) and some impurities (*).

but if their syntheses are conducted in NMR tubes, then monitoring of spectra during crystallisation of the complexes clearly reveals resonances of the binuclear complexes. The spectra are readily assigned on comparison with **1**, and are consistent with *trans*-oxidative addition; e.g. complex **2**, formed in $CDCl_3$, exhibits CH_2Pd and Me_2Pd resonances at 2.60 and 1.79 ppm, respectively, and benzene ring protons as broad resonances at 5.9 (3H) and 5.1 (1H). Complex **3**, formed in $CDCl_3$ (Fig. 1), exhibits CH_2Pd and Me_2Pd resonances at 2.62 and 1.79 ppm, together with CH_2Pt at 2.25 ppm [$^2J(^1H-^{195}Pt)$ 93 Hz], Me_2Pt at 1.36 ppm [$^2J(^1H-^{195}Pt)$ 70 Hz], and benzene ring protons as broad resonances at 5.9 (2H), 5.65 (1H) and 4.9 (1H); the $^2J(^1H-^{195}Pt)$ values are characteristic of Pt^{IV} and are identical to those reported for *fac*-$Me_2(PhCH_2)$Pt(bipy)Br [9]. In view of the marked upfield shifts of the benzene ring protons on progressing from *m*-($BrCH_2)_2C_6H_4$ (7.5–7.3 ppm) to **1** (6.8–6.4 ppm) and to **2** and **3** (5.9–4.9 ppm), complexes **1**–**3** are shown with the central benzene ring adjacent to the 2,2′-bipyridyl groups (Scheme 1).

Thus, the reactivity of Me_2Pd(bipy) toward oxidative addition by organohalides under mild conditions [1, 3–5], involving an S_N2 mechanism for iodomethane [5], appears to be applicable for the development of an extensive chemistry of palladium(IV), including binuclear Pd^{IV}–Pd^{IV} and Pd^{IV}–Pt^{IV} μ-hydrocarbyl systems.

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References

1 P. K. Byers, A. J. Canty, B. W. Skelton and A. H. White, *J. Chem. Soc., Chem. Commun.*, 1722 (1986).
2 P. K. Byers, A. J. Canty, B. W. Skelton and A. H. White, *J. Chem. Soc., Chem. Commun.*, 1093 (1987).
3 P. K. Byers, A. J. Canty, B. W. Skelton and A. H. White, *J. Organomet. Chem.*, *336*, C55 (1987).
4 P. K. Byers and A. J. Canty, *J. Chem. Soc., Chem. Commun.*, (1988), in press.
5 P. K. Byers, A. J. Canty, M. Crespo, R. J. Puddephatt and J. D. Scott, *Organometallics*, *7*, 1363 (1988).
6 W. de Graaf, J. Boersma, D. Grove, A. L. Spek and G. van Koten, *Recl. Trav. Chim. Pays-Bas*, *107*, 299 (1988).
7 M. Catellani and G. P. Chiusoli, *J. Organomet. Chem.*, *346*, C27 (1988).
8 J. D. Scott, M. Crespo, C. M. Anderson and R. J. Puddephatt, *Organometallics*, *6*, 1772 (1987); J. D. Scott and R. J. Puddephatt, *Organometallics*, *5*, 1538 (1986).
9 M. Crespo and R. J. Puddephatt, *Organometallics*, *7*, (1988), in press.