Novel *p*-Cymene-osmium(II) and -osmium(0) Complexes: a Ring Ligand determining Inter- *vs.* Intra-molecular C–H Addition

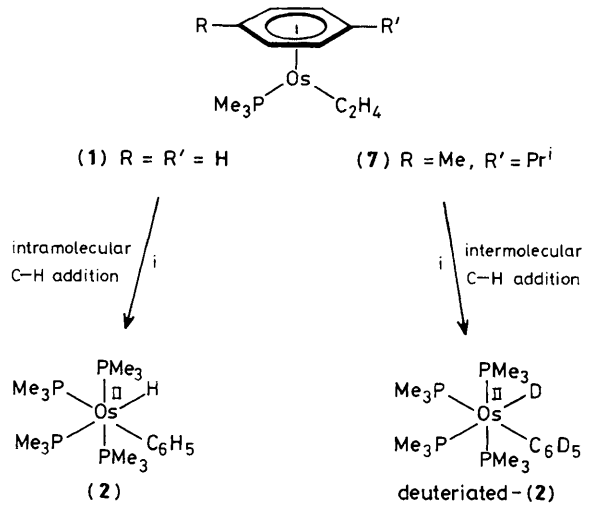
Helmut Werner* and Karin Zenkert

Institut für Anorganische Chemie der Universität Würzburg, Am Hubland, D-8700 Würzburg, Federal Republic of Germany

The osmium(0) complex [(pc)Os(C_2H_4)PMe_3] [pc = η^6-*p*-cymene (4-isopropyltoluene)] (**7**) has been prepared together with a group of neutral and cationic *p*-cymeneosmium(II) compounds; in contrast to [C_6H_6Os(C_2H_4)PMe_3], the corresponding *p*-cymene complex (**7**) reacts with an excess of PMe_3 in benzene not by intra- but by inter-molecular C–H addition to form [OsH(C_6H_5)(PMe_3)$_4$].

The factors which influence the relative ability of a transition metal complex to activate C–H bonds by an intra- or inter-molecular reaction are, as yet, poorly understood.[1] We have previously shown that the remarkably stable benzene–osmium(0) complex [C_6H_6Os(C_2H_4)PMe_3] (**1**) which is a strong metal base and thus is readily protonated to form the [C_6H_6OsH(C_2H_4)PMe_3]$^+$ cation,[2] also reacts with nucleophiles such as PMe_3 to produce the hydrido(phenyl)osmium(II) derivative *cis*-[OsH(C_6H_5)(PMe_3)$_4$] (**2**) (see Scheme 1).[3] The C–H addition in this process occurs *intra*molecularly as shown by labelling experiments.[3,4]

Further studies in this area were hampered because, in contrast to ruthenium, until recently very few areneosmium complexes having a six-membered ring other than benzene were known.[5] We report now the synthesis of a group of η^6-arene-osmium(0) and -osmium(II) compounds containing *p*-cymene as a ring ligand and describe significant differences in the C–H activation behaviour of analogous η^6-benzene- and η^6-*p*-cymene-osmium(0) derivatives. We note that very recently, Maitlis and coworkers have independently reported the preparation of (**4**) and similar *p*-cymeneosmium(II) chloro and methyl compounds;[6] a communication describing di-



Scheme 1. *Reagents:* i, 3 PMe_3, C_6D_6.

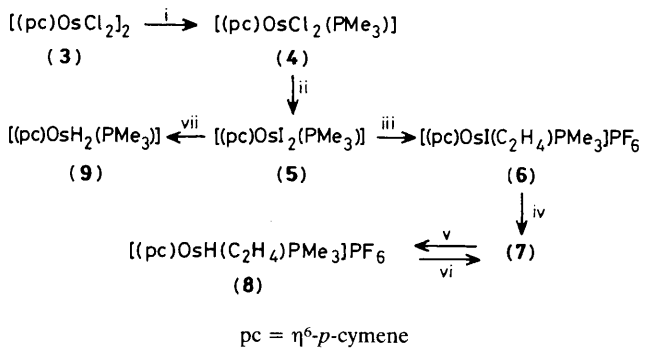
nuclear *p*-cymeneosmium(II) hydride complexes together with their ^{187}Os n.m.r. data has also appeared.[7]

Compound (**3**) may be converted to the mononuclear complex (**4**) by conventional methods (Scheme 2).[8,9] The reaction of (**4**) with $AgPF_6$ and ethylene leads to intractable products, but the ethylene complex (**6**) is obtained in good yield *via* (**5**) in which the chloride ligands have been exchanged by iodide. An ethylene atmosphere was necessary during work-up in the preparation of (**6**), in order to obtain a pure sample.

The reduction of (**6**) to produce (**7**)† follows the route which has been developed for the bis-phosphine and -phosphite derivatives $[(\eta^6\text{-ArH})ML_2]$ [M = Ru: ArH = C_6H_6, pc, C_6Me_6; M = Os: ArH = C_6H_6; L = PR_3, $P(OR)_3$];[10] it has also more recently been applied to the preparation of (**1**).[2] Compound (**7**) was purified by protonation to (**8**)† followed by regeneration of (**7**) by deprotonation with NaH. The dihydride (**9**)† was obtained from (**5**) and $NaBH_4$ *via* the route used for the benzene analogue $[C_6H_6OsH_2(PPr^i_3)]$.[11,12]

The reaction of (**7**) with an excess of trimethylphosphine in benzene surprisingly proceeds with *inter*molecular C–H addition to give the hydrido(phenyl)osmium(II) complex (**2**) accompanied by displacement of the *p*-cymene ring. This was established by n.m.r. measurements† which showed no signals for ring methyl or isopropyl protons of a *p*-$MeC_6H_3Pr^i$ group and no second hydride signal in the up-field region of the ^1H n.m.r. spectrum. Accordingly, in C_6D_6 only the deuteriated derivative *cis*-$[OsD(C_6D_5)(PMe_3)_4]$ is formed. Scheme 1 illustrates the difference in the behaviour of (**1**) and (**7**) towards PMe_3 under the same reaction conditions.

† All new compounds gave analytical data, including mass spectra, consistent with their structures. Selected spectroscopic data (complete ^1H n.m.r. data were available to the referees and can be obtained on request from the authors); i.r.: KBr, ν in cm^{-1}; n.m.r.: δ in p.p.m., *J* in Hz. (**5**): ^{31}P n.m.r. ($CDCl_3$), −61.27(s). (**6**): ^{31}P n.m.r. (CD_3NO_2), −47.03(s). (**7**): ^{31}P n.m.r. (C_6D_6), −50.24(s); ^1H n.m.r. (C_6D_6), 4.39[4H, d, *J*(H–P) 0.5, C_6H_4], 2.29[1H, sept, *J*(H–H) 6.8, $CHMe_2$], 2.17(3H, s, ring-Me), 1.67(4H, m, C_2H_4), 1.20[6H, d, *J*(H–H) 6.8, $CHMe_2$], 1.00[9H, d, *J*(H–P) 8.4, PMe_3]. (**8**): I.r., 2090 [ν(Os–H)]; ^{31}P n.m.r. [$(CD_3)_2CO$], −34.44[s, off-resonance: d, *J*(P–H) 38.0]; ^1H n.m.r. (CD_3NO_2), −13.73[1H, d, *J*(H–P) 38.0, OsH]. (**9**) I.r., 1992 [ν(Os–H)]; ^{31}P n.m.r. (C_6D_6), −46.69[s, off-resonance: t, *J*(P–H) 39.0]; ^1H n.m.r. (C_6D_6), −11.16 [2H, d, *J*(H–P) 39.0, OsH_2].



Scheme 2. *Reagents and conditions:* i, PMe_3, benzene, 70 °C, 2 h (84% yield); ii, NaI, CH_2Cl_2:MeOH 20:1, 25 °C, 6 h (100%); iii, C_2H_4, $AgPF_6$, acetone, 25 °C (58%); iv, $NaC_{10}H_8$, tetrahydrofuran (THF), −78 °C (*ca.* 60%); v, NH_4PF_6, THF, −78 °C (70%); vi, NaH, THF, 25 °C (98%); vii, $NaBH_4$, MeOH, 25 °C (80%).

To the best of our knowledge there is little precedent for a similar ligand ability to determine intra- *vs.* inter-molecular C–H addition to a transition metal. We have found that *trans*-$[RuCl_2(PMe_3)_4]$ reacts with Na/Hg in benzene to produce $[RuH(\eta^2\text{-}CH_2PMe_2)(PMe_3)_3]$ (*i.e.*, by *intra*molecular addition) whereas the bisphosphite derivative all-*trans*-$[RuCl_2(PMe_3)_2\{P(OMe)_3\}_2]$ on treatment with Na/Hg in benzene under the same conditions gives *cis,trans,cis*-$[RuH(C_6H_5)(PMe_3)_2\{P(OMe)_3\}_2]$.[13,14]

Although the benzene and *p*-cymene compounds (**1**) and (**7**) have strikingly different C–H activation properties, in many of their reactions the corresponding osmium(II) derivatives seem to be analogous. Thus, in neither case have we been able to isolate the neutral (probably highly nucleophilic) $[(\eta^6\text{-ArH})Os(PMe_3)_2]$ complex by deprotonation of the corresponding hydrido-osmium(II) cation with NaH, Bu^tLi, etc.

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References

1 J. Halpern, *Inorg. Chim. Acta*, 1985, **100**, 41; W. D. Jones and F. J. Feher, *J. Am. Chem. Soc.*, 1985, **107**, 620; A. H. Janowicz, R. A. Periana, J. M. Buchanan, C. A. Kovac, J. M. Stryker, M. J. Wax, and R. G. Bergman, *Pure Appl. Chem.*, 1984, **56**, 13.
2 R. Werner and H. Werner, *Chem. Ber.*, 1983, **116**, 2074; H. Werner and R. Werner, *J. Organomet. Chem.*, 1980, **194**, C7.
3 R. Werner and H. Werner, *Angew. Chem.*, 1981, **93**, 826; *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 793.
4 R. Werner, Ph.D. Thesis, Universität Würzburg, 1981.
5 T. Arthur and T. A. Stephenson, *J. Organomet. Chem.*, 1981, **208**, 369.
6 J. A. Cabeza and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1985, 573.
7 J. A. Cabeza, B. E. Mann, C. Brevard, and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1985, 65.
8 G. Winkhaus, H. Singer, and M. Kricke, *Z. Naturforsch., Teil B*, 1966, **21**, 1109; R. A. Zelonka and M. C. Baird, *Can. J. Chem.*, 1972, **50**, 3063; M. A. Bennett and A. K. Smith, *J. Chem. Soc., Dalton Trans.*, 1974, 233.
9 H. Werner and R. Werner, *Chem. Ber.*, 1982, **115**, 3766.
10 R. Werner and H. Werner, *Chem. Ber.*, 1982, **115**, 3781.
11 H. Kletzin, Ph.D. Thesis, Universität Würzburg, 1984.
12 K. Werner and K. Roder, *J. Organomet. Chem.*, 1985, **281**, C38.
13 H. Werner and R. Werner, *J. Organomet. Chem.*, 1981, **209**, C60.
14 H. Werner, and J. Gotzig, *J. Organomet. Chem.*, 1985, **284**, 73.