A Convenient Synthesis of Binuclear Methylpalladium(II) Complexes†

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The complexes $[Pd_2Me_2(\mu\text{-}Cl)_2(PR_3)_2]$ (R_3 = Et_3, Bu_3, Me_2Ph, $MePh_2$ or Ph_3) have been prepared by reaction of $[Pd_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ with tetramethyltin in benzene at room temperature. The complexes $[Pd_2Me_2(\mu\text{-}Cl)_2(PR_3)_2]$ react with pyrazoles in the presence of 2 mol equivalents of base to give the bis(pyrazolato)-bridged binuclear methylpalladium(II) complexes $[Pd_2Me_2(\mu\text{-}N\text{–}N)_2(PR_3)_2]$ [N–NH = pyrazole (Hpz), 3,5-dimethylpyrazole (Hdmpz), 3,4,5-trimethylpyrazole (Htmpz); PR_3 = PEt_3, PBu_3, PMe_2Ph, $PMePh_2$ or PPh_3]. The platinum analogues, $[Pt_2Me_2(\mu\text{-}N\text{–}N)_2(PMe_2Ph)_2]$, were obtained by a similar reaction. All the complexes were characterized by elemental analysis, IR and NMR (^1H, ^{13}C, ^{31}P) spectroscopy. Both chloro- and pyrazolate-bridged palladium(II) complexes adopt a *trans* configuration, whereas the platinum complexes exist as a mixture of *cis* and *trans* isomers.

The role of organopalladium compounds in a number of palladium catalysed organic transformations has now been well documented.[1,2] In general organopalladium derivatives are less stable thermodynamically and kinetically than their platinum analogues. Although organoplatinum complexes with anionic organic moieties have been known since 1907,[3] organopalladium compounds were not isolated until the 1960s.[4] The stability of an organopalladium complex depends primarily on the nature of R group and auxiliary ligands and the following stability trend is usually observed: R = perhalogenophenyl > aryl > alkyl.

Halide-bridged platinum and palladium complexes of the type $[M_2X_2(\mu\text{-}Y)_2L_2]$ (M = Pd or Pt, X = Y = halide, L = neutral donor ligand) are extremely useful synthons in the formation of mono- and bi-nuclear organometallic and coordination compounds.[5,6] Organometallic derivatives of platinum, where X = alkyl or aryl, have been studied quite extensively and have shown an interesting reaction chemistry.[6–9] However, the chemistry of the analogous palladium complexes is limited to species containing perfluorophenyl groups.[10,11] Anderson[12] has reported the synthesis of $[Pd_2R_2(\mu\text{-}Cl)_2(PR'_3)_2]$ (R = Ph or C_6H_4Me-*p*) by employing the reaction of $[Pd_2Cl_2(\mu\text{-}Cl)_2(PR'_3)_2]$ with diorganomercurials, although removal of RHgCl is a tedious process. Probably due to the non-availability of a good general synthetic method for the methyl derivatives, the chemistry of binuclear methylpalladium(II) species has remained relatively unexplored.[1,2,13]

The synthesis of binuclear alkyl complexes of the platinum group metals is of much current interest[14–16] due to their structural features and reactivity, particularly with reference to homogeneous catalysis. The pyrazolate ion and substituted pyrazolates have been proved to be a versatile ligand in constructing binuclear molecules[16–19] and in the resulting complexes the individual metal fragments are bridged by an exobidentate pyrazolate ligand. The resulting metallacyclic rings are usually puckered.

In this paper we report a convenient synthesis of the chloro-bridged methylpalladium(II) complexes $[Pd_2Me_2(\mu\text{-}Cl)_2(PR_3)_2]$ (R_3 = Et_3, Bu_3, Me_2Ph, $MePh_2$ or Ph_3). The utility of these precursors in constructing other binuclear methylpallladium(II) complexes, such as $[Pd_2Me_2(\mu\text{-}pz)_2(PR_3)_2]$ (pz = pyrazolate ion), is demonstrated. A few platinum analogues of the latter class of molecules have also been synthesized.

Experimental

The complexes $[Pd_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ (R_3 = Et_3, Bu_3, Me_2Ph, $MePh_2$ or Ph_3)[20] and $[Pt_2Me_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$[7] were prepared according to literature methods. The latter complex has been reported to contain *trans*-$[PtCl_2(PMe_2Ph)_2]$ as an impurity. Colourless crystals were mechanically separated and were recrystallized once to give spectroscopically pure $[Pt_2Me_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$. All preparations were carried out under a nitrogen atmosphere.

Elemental analyses were performed by the Analytical Chemistry Division (Bhabha Atomic Research Centre). Proton and $^{31}P\text{-}\{^1H\}$ NMR spectra were recorded in $CDCl_3$ solutions on a Bruker AMX 500 spectrometer. Chemical shifts are reported in ppm from internal $SiMe_4$ for ^1H and external 85% H_3PO_4 for ^{31}P. The $^{13}C\text{-}\{^1H\}$ NMR spectra were recorded on a Bruker AC-200 spectrometer operating at 50 MHz. Chemical shifts are reported in ppm from internal chloroform. Mass spectra were recorded on a VG Micromass 7070F instrument.

Preparation of $[Pd_2Me_2(\mu\text{-}Cl)_2(PMePh_2)_2]$.—To a benzene suspension (20 cm^3) of $[Pd_2Cl_2(\mu\text{-}Cl)_2(PMePh_2)_2]$ (503 mg, 0.67 mmol), an excess of tetramethyltin (0.4 cm^3, 2.89 mmol) was added and the whole was stirred at room temperature for 1 h (20 min for the triethylphosphine, tributylphosphine and dimethylphenylphosphine complexes; 1.5 h for the triphenylphosphine complex) (longer stirring tends to give palladium metal) until a clear colourless to pale yellow solution was obtained. The odour of $SnMe_3Cl$ was detectable. The solvent and organotins ($SnMe_4$, $SnMe_3Cl$) were removed *in vacuo*. The residue was extracted with benzene, passed through a Florisil column and the volume was reduced to 2 cm^3. To this was added hexane (5 cm^3) and on cooling cream crystals of the product (356 mg, 75%) were obtained. The other chloro-bridged methylpalladium complexes were prepared similarly.

Preparation of $[Pd_2Me_2(\mu\text{-}dmpz)_2(PMe_2Ph)_2]$ (dmpz = *3,5-dimethylpyrazolate*).—To a benzene (10 cm^3) suspension of $[Pd_2Cl_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$ (200 mg, 0.32 mmol), tetramethyltin (90 µl, 0.66 mmol) was added and the whole was stirred for

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† *Supplementary data available* (No. SUP 56943, 3 pp.): ^1H NMR data. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Analytical and physical data for $[M_2Me_2(\mu\text{-}Y)_2(PR_3)_2]$ (M = Pd or Pt; Y = Cl or N–N)

Complex	Solvent of recrystallization (% yield)	M.p./°C	Analysis[a] (%) C	H	N	$\delta(^{31}P)$[b]	δ(M–Me)[c]
$[Pd_2Me_2(\mu\text{-Cl})_2(PEt_3)_2]$	Benzene–hexane (73)	84	30.1 (30.6)	6.5 (6.6)	—	30.3	0.56 (br)
$[Pd_2Me_2(\mu\text{-pz})_2(PEt_3)_2]$	Benzene–hexane (55)	139	39.6 (39.2)	6.7 (6.9)	8.7 (9.1)	24.4	0.24 (d, 3.7)
$[Pd_2Me_2(\mu\text{-dmpz})_2(PEt_3)_2]$	Benzene–hexane (55)	159	42.9 (43.1)	7.3 (7.5)	7.9 (8.4)	23.1	0.24 (d, 4.2)
$[Pd_2Me_2(\mu\text{-Cl})_2(PBu_3)_2]$	Hexane (68)	67	43.5 (43.3)	8.4 (8.4)	—	22.2	0.56 (br)
$[Pd_2Me_2(\mu\text{-pz})_2(PBu_3)_2]$	Hexane (60)	92	49.7 (49.2)	9.0 (8.5)	7.8 (7.2)	16.2	0.24 (d, 3.8)
$[Pd_2Me_2(\mu\text{-pz})_2(PMe_2Ph)_2]$	Benzene–hexane (61)	125	44.5 (44.1)	5.1 (5.2)	7.9 (8.5)	3.8	0.35 (d, 4.3)
$[Pt_2Me_2(\mu\text{-pz})_2(PMe_2Ph)_2]$	CH_2Cl_2–EtOH (71)	134	34.6 (34.7)	4.1 (4.1)	6.6 (6.7)	−17.2 (4000)[d] −18.0 (3909)[e]	0.51 (d, 4.3, *cis*) 0.53 (d, 4.3, *trans*)
$[Pd_2Me_2(\mu\text{-dmpz})_2(PMe_2Ph)_2]$	Benzene–hexane (55)	155[f]	47.0 (47.4)	5.8 (6.0)	7.6 (7.9)	4.7	0.30 (d, 4.7)
$[Pt_2Me_2(\mu\text{-dmpz})_2(PMe_2Ph)_2]$	CH_2Cl_2–EtOH (66)	164	37.4 (37.9)	4.7 (4.8)	6.1 (6.3)	−16.8 (br, 4056)	0.47 (d, 4.5, *cis*) 0.50 (d, 4.5, *trans*)
$[Pd_2Me_2(\mu\text{-tmpz})_2(PMe_2Ph)_2]$	Benzene–hexane (55)	142[f]	48.5 (48.9)	6.2 (6.3)	7.0 (7.6)	4.3	0.27 (d, 4.8)
$[Pt_2Me_2(\mu\text{-tmpz})_2(PMe_2Ph)_2]$	CH_2Cl_2–EtOH (68)	203	39.3 (39.4)	5.1 (5.0)	6.1 (6.1)	−17.1 (br, 4031,[d] 3960)	0.43 (d, 4.5 *cis*) 0.47 (d, 4.7, *trans*)
$[Pd_2Me_2(\mu\text{-Cl})_2(PMePh_2)_2]$	Benzene–hexane (75)	118–120[f]	46.3 (47.1)	4.4 (4.5)	—	21.6	0.60 (br)
$[Pd_2Me_2(\mu\text{-pz})_2(PMePh_2)_2]$	Benzene–hexane (60)	105	52.1 (52.5)	4.8 (4.9)	6.7 (7.2)	19.5	0.34 (d, 4.3)
$[Pd_2Me_2(\mu\text{-dmpz})_2(PMePh_2)_2]$	Benzene–hexane (59)	209[f]	54.1 (54.7)	5.2 (5.5)	6.7 (6.7)	19.2	0.37 (d, 4.7)
$[Pd_2Me_2(\mu\text{-tmpz})_2(PMePh_2)_2]$	Benzene–hexane (57)	202[f]	55.4 (55.7)	5.8 (5.8)	6.1 (6.5)	19.1	0.32 (d, 4.9)
$[Pd_2Me_2(\mu\text{-Cl})_2(PPh_3)_2]$	CH_2Cl_2–hexane (35)	110–114[f]	53.9 (54.4)	4.3 (4.3)	—	37.0	0.64 (br)
$[Pd_2Me_2(\mu\text{-pz})_2(PPh_3)_2]$	Benzene–hexane (59)	183–185[f]	58.7 (58.6)	4.3 (4.7)	6.3 (6.2)	26.8	0.35 (d, 4.3)
$[Pd_2Me_2(\mu\text{-dmpz})_2(PPh_3)_2]$	Benzene–hexane (57)	159–161[f]	59.1 (60.2)	5.3 (5.3)	4.8 (5.8)	31.8	0.34 (d, 4.6)

[a] Required values are given in parentheses. [b] Values in parentheses are $^1J(^{195}Pt-^{31}P)$ in Hz. [c] Values in parentheses are $^3J(^{31}P-^1H)$ in Hz. [d] For *cis* isomer. [e] For *trans* isomer. [f] With decomposition.

10 min during which a colourless solution was formed. The solvent was evaporated *in vacuo* and the residue was washed with hexane and dried. The cream solid, $[Pd_2Me_2(\mu\text{-Cl})_2(PMe_2Ph)_2]$, was suspended in methanol (20 cm^3). To this was added 3,5-dimethylpyrazole (61 mg, 0.63 mmol) in methanolic (5 cm^3) sodium hydroxide (650 μl, 0.98 mol dm^{-3}, 0.64 mmol) with vigorous stirring. The reactants were stirred for 5 h at room temperature. The solvent was removed *in vacuo* and the residue was extracted with benzene (3 × 5 cm^3). The solvent was reduced to 2 cm^3 and hexane (5 cm^3) was added and on cooling gave colourless crystals of the product (124 mg, 55%). Similar reactions of $[M_2Me_2(\mu\text{-Cl})_2(PR_3)_2]$ (M = Pd or Pt) with pyrazoles in the presence of sodium hydroxide yielded bis(pyrazolato)-bridged complexes. Pertinent data for these complexes are given in Table 1.

$^{13}C-\{^1H\}$ NMR ($CDCl_3$): $[Pd_2Me_2(\mu\text{-pz})_2(PEt_3)_2]$, δ −6.9 (d, 7.5, Pd–Me), 8.1 (s, CH_2CH_3), 15.5 (d, 29 Hz, PCH_2), 102.7 (s), 135.6 (s) and 137.3 (s) (pz). $[Pd_2Me_2(\mu\text{-tmpz})_2(PMe_2Ph)_2]$, δ −7.5 (d, 8.7, Pd–Me), 12.6 (d, 11, PMe_2), 14.6 (d, 11, PMe_2), 8.8 (s), 14.1 (s), 15.1 (s) ($C_3N_2Me_3$), 102.8 (s), 136.4 (s), 135.5 (s) ($C_3N_2Me_3$), 128.2 (d, 7.7), 129.8 (s), 131.6 (d, 11 Hz) and 142.8 (s) (Ph).

Results and Discussion

Treatment of the complexes $[Pd_2Cl_2(\mu\text{-Cl})_2(PR_3)_2]$ with tetramethyltin in benzene solution afforded the chloro-bridged binuclear methylpalladium(II) species $[Pd_2Me_2(\mu\text{-Cl})_2(PR_3)_2]$. The reaction of these complexes with pyrazoles in 1:2 stoichiometry in the presence of 2 mol equivalents of sodium hydroxide gave exclusively bis(pyrazolato)-bridged species, $[Pd_2Me_2(\mu\text{-N-N})_2(PR_3)_2]$ [equation (1): N–NH = pyrazole

$$\begin{array}{l} [Pd_2Cl_2(\mu\text{-Cl})_2(PR_3)_2] + 2SnMe_4 \longrightarrow \\ \qquad [Pd_2Me_2(\mu\text{-Cl})_2(PR_3)_2] + 2SnMe_3Cl \\ \qquad \quad \Big\downarrow \text{2N-NH + 2NaOH} \\ \qquad [Pd_2Me_2(\mu\text{-N-N})_2(PR_3)_2] + 2NaCl \end{array} \quad (1)$$

(Hpz), 3,5-dimethylpyrazole (Hdmpz) or 3,4,5-trimethylpyrazole (Htmpz); $PR_3 = PEt_3$, PBu_3, PMe_2Ph, $PMePh_2$ or PPh_3]. A few platinum analogues [equation (2)] of the latter species

$$\begin{array}{l} [Pt_2Me_2(\mu\text{-Cl})_2(PMe_2Ph)_2] + 2N\text{-}NH + 2NaOH \longrightarrow \\ \qquad [Pt_2Me_2(\mu\text{-N-N})_2(PMe_2Ph)_2] + 2NaCl \end{array} \quad (2)$$

have also been prepared by similar reactions to compare the properties of the two series of complexes.

The chloro-bridged methylpalladium(II) complexes are cream crystalline solids and are found to darken at room temperature after 2–3 weeks. The pyrazolato-bridged complexes are white crystalline solids which remain apparently unchanged over a period of several months.

The chloro-bridged complexes $[Pd_2Me_2(\mu\text{-Cl})_2(PR_3)_2]$ exhibited a single resonance in their ^{31}P NMR spectra. The ^1H

NMR spectra displayed a broad resonance at δ ≈0.6 attributable to the Pd–Me protons. These data suggest that only one isomer, *sym-cis* or *sym-trans*, is formed exclusively. Possibly there is rapid isomerization between the *cis* and *trans* forms leading to the observed broad Pd–Me resonance, although for analogous platinum complexes both *cis* and *trans* isomers coexist in solution.[7,9] The presence of only one strong band in the region 250–265 cm^{-1} assignable to the ν(Pd–Cl) stretching vibration indicates that these molecules adopt a *sym-trans* configuration.[9,21] It is noteworthy that the analogous platinum complexes $[Pt_2R'_2(\mu\text{-}Cl)_2(PR_3)_2]$ (R′ = Me or aryl, $R_3 = Et_3$ or Me_2Ph) exist as a mixture of *cis* and *trans* isomers.[7,9]

The ^{31}P NMR spectra of the $[Pd_2Me_2(\mu\text{-}N\text{-}N)_2(PR_3)_2]$ complexes displayed a single resonance indicating the presence of only one isomeric form. However, the platinum complexes exhibited two such resonances each with platinum satellites. The resonance with the larger coupling constant is assigned to the *cis* isomer and the signal with the smaller ^1J(Pt–P) is attributed to the *trans* isomer.[8] The resonances for the bis(pyrazolato)-bridged palladium and platinum complexes are considerably shielded with respect to those observed for the corresponding $[M_2Me_2(\mu\text{-}Cl)_2(PR_3)_2]$ (M = Pd or Pt) complexes.

The ^1H NMR spectra (SUP 56943) exhibited the expected integration and peak multiplicities. The palladium complexes showed a doublet for the Pd–Me protons with ^3J(P–H) ≈ 4 Hz. Similarly in the ^{13}C NMR spectra the Pd–Me carbon appeared as a doublet with ^2J(P–C) ≈ 8 Hz. For the mononuclear species *trans*-$[PdMe_2(PPh_3)_2]$[22] ^2J(P–C) has been reported to be 16 Hz. The ^1H NMR spectra of the platinum complexes $[Pt_2Me_2(\mu\text{-}N\text{-}N)_2(PMe_2Ph)_2]$ showed two doublets attributable to the Pt–Me protons of the *cis* and *trans* isomers. The ^3J(P–H) values for these complexes are comparable to those of the corresponding palladium species. The ratio of two isomers varied from one preparation to another.

The palladium complexes exhibited only one resonance for the C^4 substituent of the pyrazolate ring in the ^1H and ^{13}C NMR spectra. This suggests that the palladium complexes adopt a *sym-trans* configuration. The *cis* isomer would give rise to two such resonances due to non-equivalence of the two pyrazolate rings. Since the platinum complexes are formed as a mixture of *cis* and *trans* isomers, three resonances for the C^4 substituents are observed in their ^1H NMR spectra.

The mass spectra of $[Pd_2Me_2(\mu\text{-}pz)_2(PR_3)_2]$ ($PR_3 = PEt_3$ or PMe_2Ph) showed a complex molecular ion peak at *m/z* 614 (PEt_3) and 654 (PMe_2Ph). A complex pattern is expected due to two polyisotopic palladium atoms present in the dimeric species. The spectra showed a most abundant peak due to $[Pd_2Me(\mu\text{-}pz)_2(PR_3)_2]^+$ formed by loss of one methyl group.

Acknowledgements

Thanks are due to Dr. J. P. Mittal for his encouragement and interest in this work. We are grateful for the use of the 500 MHz National NMR facility at the Tata Institute of Fundamental Research to obtain the NMR spectra and the Head of the Analytical Chemistry Division (Bhabha Atomic Research Centre) for microanalysis.

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Received 23*rd December* 1992; *Paper* 2/06809E