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DIMETHYLMETAL(III) PYRAZOLIDES

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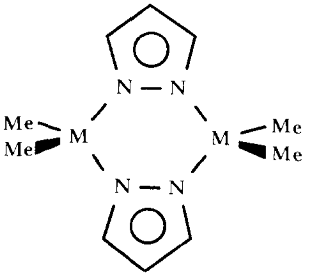
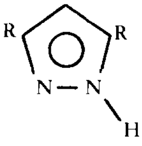
Summary

The complexes $Me_2Au(R_2pz)$ (R = H, Me; pzH = pyrazole) are formed on reaction of dimethylgold(III) nitrate with 3,5-disubstituted pyrazoles, R_2pzH, in water, but a similar procedure with Ph_2pzH followed by recrystallization from $CHCl_3/CCl_4$ gives $[Me_2Au(Ph_2pzH)_2]NO_3 \cdot$ ca.$\frac{3}{4}CCl_4$. The complexes $Me_2M(Ph_2pz)$ (M = Au, Tl), $Me_2In(Ph_2pz) \cdot 1/2CH_2Cl_2$, and $Me_2Tl(Me_2pz)$ are formed on reaction of Me_2MI (M = Au, Tl) or Me_2InCl with $Ag(R_2pz)$ in non-aqueous solvents. The complexes $Me_2Au(R_2pz)$ (R = H, Me, Ph) are dimeric in chloroform and $Me_2Tl(Me_2pz)$ is dimeric in benzene, but osmometric data for $Me_2Tl(Ph_2pz)$ in benzene indicate presence of a monomer–dimer equilibrium.

Pyrazoles may act as unidentate ligands [1], but are of particular interest as deprotonated bridging ligands in the synthesis of polynuclear complexes [1,2]. The interaction of simple organometal and organometalloidal groups with pyrazoles has been extensively studied only for the Group III elements [1,3–11], for which dimeric structures have been established for pyrazaboles, e.g. $[Et_2B(Me_2pz)]_2$ [4], and derivatives containing aluminium [6] and gallium [6–8], e.g. $[Me_2M(pz)]_2$, and indicated from spectroscopic data for thallium [11]. For these molecules distorted tetrahedral geometry for the metal atom is expected. We report here studies of the interaction of pyrazoles R_2pzH with Me_2Au^{III} where, in contrast, square-planar coordination is expected. Isolation of $[Me_2Au(Ph_2pzH)_2]NO_3 \cdot$ ca.$\frac{3}{4}CCl_4$ under





R_2pzH

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TABLE 1

ANALYTICAL, MOLECULAR WEIGHT, AND ^{1}H NMR DATA FOR Me_2M^{III} COMPLEXES OF PYRAZOLES

Complex	Analysis (Found (calcd.) (%))			Molecular weight data [a]		^{1}H NMR data [b]			Solvent for Mol. wt. and NMR
	C	H	N	Found/Calcd. (n)	Temp. (°C)	$\delta(Me_2M)$	δ(H(4))	δ(R)	
$Me_2Au(pz)$	20.5 (20.4)	3.3 (3.1)	9.4 (9.5)	2.02,1.93	37	1.08s	6.35b	7.44b	chloroform
$Me_2Au(Me_2pz)$	26.2 (26.1)	4.2 (4.1)	8.6 (8.7)	1.98,1.94	37	1.02s	5.88s	2.20s	chloroform
$Me_2Au(Ph_2pz)$	45.6 (45.7)	3.9 (3.8)	6.5 (6.3)	1.97,1.95	37	0.63s	6.82s	7.90m [c] 7.45m [d]	chloroform
$[Me_2Au(Ph_2pzH_2]\cdot NO_3$ ca. $\frac{3}{4}CCl_4$ [e,f]	46.4 (46.5)	3.4 (3.6)	8.3 (8.3)	–		1.14s	6.76s [g]	7.76m [c] 7.38m [d]	chloroform
$Me_2Tl(Me_2pz)$	26.4 (25.5)	4.4 (4.0)	8.7 (8.5)	2.03,1.95	60	0.80d [h,i]	5.78s	2.08s	benzene
$Me_2Tl(Ph_2pz)$	45.2 (45.0)	3.9 (3.8)	6.4 (6.2)	1.48,1.45 1.64,1.61 1.82,1.77	60 45 37	0.74d [h,j]	6.74s	7.64m 7.15m	benzene
$Me_2In(Ph_2pz)\cdot$ ca. $\frac{1}{2}CH_2Cl_2$ [e,k]	52.2 (51.7)	4.7 (4.5)	7.3 (6.9)	–	–	–	–	–	–

[a] Determined osmometrically. [b] Chemical shifts from Me_4Si, with integration appropriate for formulae presented. [c] H(2,6). [d] H(3,4,5). [e] High resolution mass spectrum confirms the presence of solvate (Experimental). [f] $\nu(NO_3^-)$ 1329 vs cm^{-1} (KBr disk). [g] δ(NH) 14.2s. [h] $|^2J(^1H-^{203}Tl)|$ and $|^2J(^1H-^{205}Tl)|$ not resolved. [i] $|^2J(^1H-Tl)|$ 383 Hz. [j] $|^2J(^1H-Tl)|$ 375 Hz. [k] Insoluble.

conditions giving $[Me_2Au(R_2pz)]_2$ (R = H, Me) has lead to an examination of the interaction of Ph_2pz^- with the Group III cations dimethylthallium(III) and dimethylindium(III).

Results and discussion

Aqueous solutions of dimethylgold(III) nitrate react readily with R_2pzH (R = H, Me) to form pyrazolide complexes, but Ph_2pzH gives a complex involving coordination of the parent pyrazole (eq. 1 and 2). The complexes were recrystallized from

$$Me_2Au^+ + R_2pzH \xrightarrow{H_2O} Me_2Au(R_2pz)\downarrow + H^+ \quad (1)$$

(R = H, Me)

$$Me_2Au^+ + 2Ph_2pzH \xrightarrow{H_2O} [Me_2Au(Ph_2pzH)_2]^+ \quad (2)$$

organic solvents, giving a solvate for the ionic complex, $[Me_2Au(Ph_2pzH)_2]NO_3 \cdot$ ca. $\frac{3}{4}CCl_4$.

In order to obtain a 3,5-diphenylpyrazolide complex, dimethylgold(III) iodide was treated with $Ag(Ph_2pz)$, and this procedure was extended to include dimethylthallium(III) derivatives of Ph_2pz^- and Me_2pz^- (eq. 3). The complexes have

$$Me_2MI + Ag(R_2pz) \rightarrow Me_2M(R_2pz) + AgI\downarrow \quad (3)$$

M = Au, R = Ph (in chloroform); M = Tl, R = Me, Ph (in benzene)

appropriate microanalyses and ^1H NMR spectra (Table 1).

As the synthesis of $Me_2Au(Ph_2pz)$ required conditions precluding formation of Ph_2pzH, we assume that in water the cation $[Me_2Au(Ph_2pzH)_2]^+$ is favoured owing to less steric crowding involving Me. . . Ph interactions in the cation compared with the dimeric structure expected for $Me_2Au(R_2pz)$. In view of this, the established dimeric structure of $[Cl_2Au(4\text{-}Cl,Ph_2pz)]_2$ in chloroform [12], and trimeric structures for some inorganic pyrazolides [13], molecular weight data were obtained to determine n for $[Me_2Au(R_2pz)]_n$, and compared with complexes of Me_2Tl^{III} and Me_2In^{III} where the metal atoms have a quite different characteristic coordination geometry, and thus different expected intramolecular Me. . . R interactions.

All of the Me_2Au^{III} complexes are found to be dimeric in chloroform at 37°C (Table 1) and $Me_2Tl(Me_2pz)$ is dimeric in benzene at 60°C, but $Me_2Tl(Ph_2pz)$ gives molecular weight values consistent with the presence of monomers in equilibrium with higher oligomers, presumably dimers.

$$[Me_2Tl(Ph_2pz)]_2 \rightleftarrows 2Me_2Tl(Ph_2pz) \quad (4)$$

The dimethylindium(III) derivative $Me_2In(Ph_2pz) \cdot$ ca. $\frac{1}{2}CH_2Cl_2$ was found to be highly insoluble and unsuitable for solution studies.

Experimental

^1H NMR spectra were recorded on a JEOL JNM-4H-100 spectrometer, mass spectra were determined with a VG 7070F spectrometer, and molecular weights were determined with a Knauer vapour phase osmometer calibrated with benzil solutions. Microanalyses were by the Australian Microanalytical Service, Melbourne. The ligands pyrazole (Fluka), 3,5-dimethylpyrazole (Fluka), and 3,5-diphenylpyrazole (Columbia) were used as received, and dimethylmetal(III) iodides were prepared as described [14–16].

$Me_2Au(pz)$, $Me_2Au(Me_2pz)$, *and* $[Me_2Au(Ph_2pzH)_2]NO_3 \cdot ca. \frac{3}{4}CCl_4$

To aqueous solutions of dimethylgold(III) nitrate, prepared as described [17], aqueous solutions of an equimolar quantity of the pyrazoles were added. White precipitates formed immediately, and these were collected, washed with water, dried, recrystallized from organic solvents and dried at ambient temperature under high vacuum, giving $Me_2Au(pz)$ (recrystallized from methanol, 46% yield), $Me_2Au(Me_2pz)$ (1/1 acetone/methanol, 50%), and $[Me_2Au(Ph_2pzH)_2]NO_3 \cdot ca. \frac{3}{4}CCl_4$ (1/1 chloroform/carbon tetrachloride, 59%), as white powders. The Ph_2pzH complex gives a mass spectrum (decomposition) showing a peak characteristic of carbon tetrachloride, *m/e* 116.906 (lit. [18] 116.9065 for CCl_3^+).

$Me_2Au(Ph_2pz)$

On addition of 3,5-diphenylpyrazolatosilver(I) (0.2553 g, 0.780 mmol), prepared similarly to other silver(I) pyrazolides [19], to a solution of dimethylgold(III) iodide (0.2737 g, 0.773 mmol) in chloroform (20 ml) in the absence of light, a yellow-precipitate formed immediately. The silver iodide was removed by filtration, and on slow evaporation to low volume a white solid formed and was collected (0.095 g, 28%).

$Me_2Tl(Me_2pz)$ *and* $Me_2Tl(Ph_2pz)$

In a similar procedure to that above dimethylthallium(III) iodide and pyrazolatosilver(I) salts were added to dry benzene in a 100 ml three-necked flask fitted with a reflux condenser, magnetic stirrer, and nitrogen atmosphere. The suspension was refluxed with stirring until a yellow precipitate of silver iodide was observed, refluxed for a further hour, and cooled to ambient temperature. The AgI and excess Me_2TlI were removed by filtration through celite under nitrogen, and the filtrate reduced to dryness under vacuum. $Me_2Tl(Me_2pz)$ was sublimed in a vacuum at 120°C prior to molecular weight determinations, and $Me_2Tl(Ph_2pz)$ was purified under nitrogen by dissolution in hot petroleum (b.p. 62–68°C), filtration, and reduction to low volume to give a white solid.

$Me_2In(Ph_2pz) \cdot 1/2CH_2Cl_2$

In a similar procedure dimethylindium(III) chloride and 3,5-diphenylpyrazolatosilver(I) were stirred in dry dichloromethane at ambient temperature until a white, fluffy, precipitate of silver chloride was observed. The AgCl and excess Me_2InCl were removed by filtration through celite under nitrogen, and the filtrate reduced to dryness under vacuum, giving an off-white solid with a mass spectrum (decomposition) showing a peak characteristic of dichloromethane, *m/e* 48.9845 (lit. [18] 48.9845 for CH_2Cl^+).

Acknowledgements

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