actually diminish the strength of any possible Cl→Ta π bonding. However, in the SAP conformation the d electron would presumably occupy the d_{z^2} orbital, which is the uniquely σ-nonbonding orbital but also a potentially Ta–P bonding orbital. Thus, by a relatively small rearrangement of the coordination sphere, in which ligand–ligand repulsive forces would not be much changed, an appreciable increase in π bonding might be secured. This is our current best hypothesis to explain the DD → SAP conformational change observed in the $[TaCl_4(dmpe)_2]^+ \rightarrow TaCl_4(dmpe)_2$ reduction.

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Supplementary Material Available: Tables of anisotropic thermal vibration tensor components and structure factors for both structures (9 pages). Ordering information is given on any current masthead page.

Contribution from the Departments of Chemistry, University of Alabama, University, Alabama 35486, and University of Victoria, Victoria, British Columbia, Canada V8W 2Y2

Crystal and Molecular Structures of Tetrafluoroborate Salts of the *cis*-Chlorobis(triethylphosphine)(3-(trifluoromethyl)-5-methylpyrazole)platinum(II) and *cis*-Chlorobis(triethylphosphine)(indazole)platinum(II) Cations

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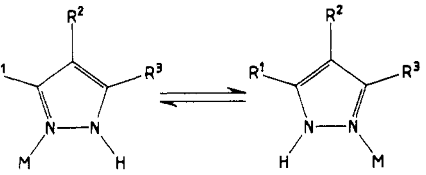
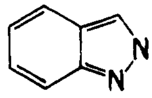
Full X-ray crystallographic data are reported for the Pt(II) cations *cis*-$[PtCl(PEt_3)_2(MTMP)]^+$ (**1**) and *cis*-$[PtCl(PEt_3)_2(INN)]^+$, acetone monosolvate (**3**) of **2**, MTMP = methyl(trifluoromethyl)pyrazole and INN = indazole, both as BF_4^- salts. The Pt–N distances are short compared with those in related cations at 1.95 (3) and 1.96 (3) Å, respectively. In **1** MTMP is bonded to Pt through N^2, i.e., complexation of 3-(trifluoromethyl)-5-methylpyrazole, while in **2** INN is bound via the N^2 nitrogen as expected. It is suggested on the basis of ^{13}C NMR spectroscopy that neutral MTMP exists in solution as $(3\text{-}CF_3)(5\text{-}CH_3)C_3N_2H_2$. Accordingly, deprotonation of MTMP or INN provides access to the neutral pyrazolyl–Pt(II) complexes *cis*-$Pt(PEt_3)_2L_2$, ^{13}C and ^{31}P NMR data for the first of which indicate that the product is an isomer in which the Me (rather than the CF_3) substituent of the MTMP heterocycle is closest to Pt.

Earlier we discussed[2a] the nature of the processes that give rise to temperature-dependent ^1H and ^{31}P NMR spectra in cationic palladium(II) complexes incorporating pyrazoles as neutral unidentate ligands. In these systems the fast limit for rearrangement behavior is characterized by equivalence among the N^1 and N^2 sites (eq 1) for $R^1 = R^3$. We also noted that



A B (1)

the corresponding platinum(II) complexes are nonfluxional and presented details of the crystal and molecular structure of *cis*-$[PdCl(PEt_3)_2L][BF_4]$ for L = 3,5-dimethylpyrazole. Coordination of a neutral, unsymmetrical pyrazole (i.e., $R^1 \neq R^3$) in a related fashion leads, however, to the situation in which A and B are not identical although they are isomeric, and the exchange represented by eq 1 is nondegenerate, rather than degenerate. In this context we have investigated ligation to Pd or Pt of methyl(trifluoromethyl)pyrazole (MTMP) and indazole (INN). In the first case for the R^1 = Me, $R^3 = CF_3$ configuration A represents a 3-methyl-5-(trifluoromethyl)pyrazole complex while B is the corresponding 3-trifluoromethyl-5-methyl species: similarly, when A implies complexation by INN, then B is a complex of the nonbenzenoid isomer 2*H*-indazole (2*H*-INN), C. Characterization by X-ray



C

crystallography of the cationic platinum(II) complexes *cis*-$[PtCl(PEt_3)_2L][BF_4]$, where L = MTMP and INN, forms the substance of the present paper. Transition-metal complexes of MTMP have not been reported previously, and indeed very little of the chemistry of this compound has been investigated despite its straightforward access from the reaction of 1,1,1-trifluoroacetylacetone with hydrazine.[2b] A limited range of transition-metal complexes of INN are known,[3] but none of 2*H*-INN are known. For comparative purposes the formation from the deprotonated heterocycles of platinum(II)-methyl(trifluoromethyl)pyrazolyl and -indazolyl complexes has also been cursorily examined.

Experimental Section

Synthetic, analytical, and instrumental procedures and preparation of starting materials have been detailed in a previous paper.[2a] The ^{13}C NMR spectrum of MTMP and one Pt(II) complex were measured at 62.89 MHz with a Bruker WM250 spectrometer.

***cis*-$[PtCl(PEt_3)_2(MTMP)][BF_4]$ (1).** To a solution of $[Pt_2Cl_2(PEt_3)_4][BF_4]_2$ (0.17 g, 0.15 mmol) in acetone (15 cm^3) was added $C_5H_5N_2F_3$ (MTMP, 0.045 g, 0.30 mmol) in the same solvent (10 cm^3). The colorless solution was stirred at ambient temperature (5 h), the solvent removed, and the residue crystallized from CH_2Cl_2/pentane to give the product **1** (0.14 g, 70%).

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(1) (a) University of Alabama. (b) University of Victoria.

(2) (a) G. W. Bushnell, K. R. Dixon, D. T. Eadie, and S. R. Stobart, *Inorg. Chem.*, **20**, 1545 (1981). (b) By a procedure similar to that described for 3,5-bis(trifluoromethyl)pyrazole: S. Trofimenko, *J. Am. Chem. Soc.*, **89**, 3170 (1967).

(3) (a) S. A. A. Zaida, A. S. Farooqi, and N. Singhal, *Acta Chim. Acad. Sci. Hung.*, **94**, 51 (1977); (b) J. A. C. Van Ooijen and J. Reedjik, *J. Magn. Magn. Mater.*, **12**, 1 (1979); (c) S. A. A. Zaida, N. Singhal, and A. Lal, *Transition Met. Chem. (Weinheim, Ger.)*, **4**, 133 (1979).

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***cis*-$[PtCl(PEt_3)_2(INN)][BF_4]$ (2).** This complex was prepared in a manner identical with that described above for **1**, with INN in place of MTMP. Recrystallization from acetone afforded the acetone monosolvate **3**, which was the subject of the crystallographic structure determination.

***cis*-$Pt(PEt_3)_2(NCMeCHC(CF_3)N)_2$ (4).** To a solution of *cis*-$PtCl_2(PEt_3)_2$ (0.25 g, 0.5 mmol) and MTMP (0.15 g, 1.0 mmol) in methanol (60 cm^3) was added KOH (0.3 g, excess) in methanol (25 cm^3). After stirring (1 h) and removal of solvent, the residue was extracted with CH_2Cl_2 (50 cm^3), and the extract was filtered and concentrated to 5 cm^3. Addition of pentane and cooling afforded the product **4** as white blocklike crystals (0.25 g, 70%).

***cis*-$Pt(PEt_3)_2(C_7H_5N_2)_2$ (5).** The bis(indazolyl) complex was obtained as above, with use of INN instead of MTMP.

X-ray Data Collection and Structure Determination. $[PtCl(PEt_3)_2(MTMP)][BF_4]$ (1). A platelike crystal of the air-stable compound, obtained by slow diffusion of Et_2O into an acetone solution, was sealed in a thin-walled glass capillary. Final lattice parameters, as determined from a least-squares refinement of the angular settings for 15 reflections ($\theta > 18°$) accurately centered on an Enraf-Nonius CAD-4 diffractometer, are given in Table I.

Data were collected with use of the parameters presented in Table I, and 2762 reflections were considered observed ($I > 3\sigma(I)$). The intensities were corrected for Lorentz, polarization, and absorption effects.

The position of the platinum atom was revealed after Patterson map inspection, and the difference Fourier phased on the metal led to the coordinates of the remaining non-hydrogen atoms. Full-matrix least-squares refinement was carried out with the SHELX program series.[4] After several cycles of least-squares refinement with isotropic, and then later anisotropic, thermal parameters, final values of $R = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.067$ and $R_w = [\sum(|F_o| - |F_c|)^2/\sum(F_o)^2]^{1/2} = 0.077$ were observed. Unit weights were used throughout the refinement. The largest parameter shifts in the final cycle were less than 0.05 of their standard deviations, and no unaccounted electron density was shown by the final difference Fourier map. Atomic scattering factors for Pt, Cl, P, F, N, and C were taken from Cromer and Mann,[5] whereas those for H were taken from ref 6. Correction for the real and imaginary components of anomalous dispersion were used for Pt.[7]

$[PtCl(PEt_3)_2(INN)][BF_4]\cdot(CH_3)_2CO$ (3). A platelike single crystal of the compound, **3**, was mounted and sealed in a thin-walled glass capillary. With the same procedures followed as for **1**, unit cell dimensions were accurately determined, and the resulting dimensions are given in Table I. The parameters used in data collection are presented also in Table I, and 2030 independent observed reflections were collected. The procedure for structure determination and refinement was the same as for **1**, but only Pt, Cl, and the two P atoms were refined anisotropically. Difficulties in refinement at this point, which might be attributed to absorption or scaling problems from the loss in intensity during data collection, prevented the refinement of the remaining non-hydrogen atoms with anisotropic thermal parameters. (At the end of data collection the crystal scattered so poorly that an empirical absorption correction could not be applied.) At this point the R values were $R = 0.127$ and $R_w = 0.131$. The largest parameter shifts in the cationic part of the species were less than 0.05 of their estimated standard deviations, with slightly higher shifts being observed in the anion and solvent molecule. There were no unaccounted electron densities.

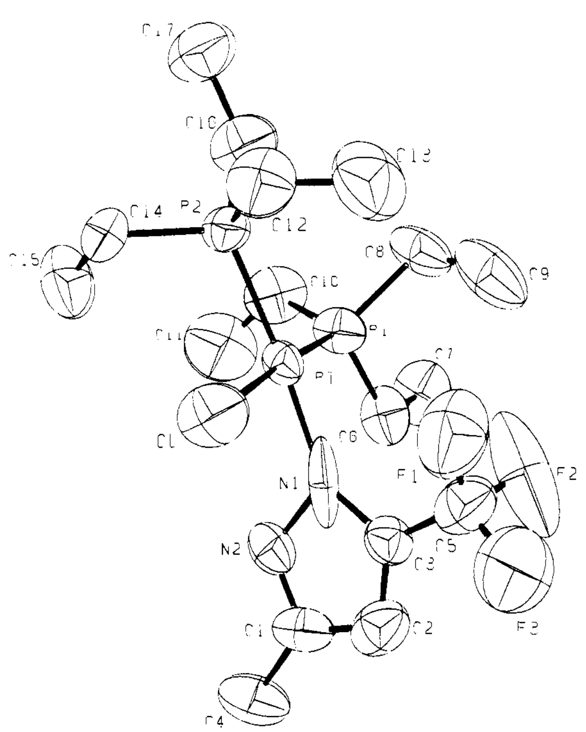

Figure 1. Molecular structure of *cis*-$[PtCl(PEt_3)_2(MTMP)][BF_4]$ (cation only).

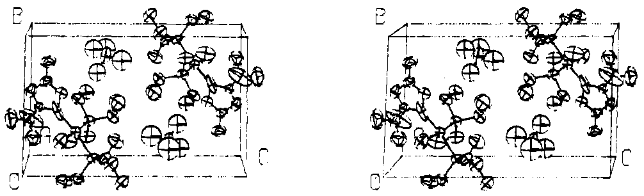

Figure 2. Crystal packing arrangement for *cis*-$[PtCl(PEt_3)_2(MTMP)][BF_4]$.

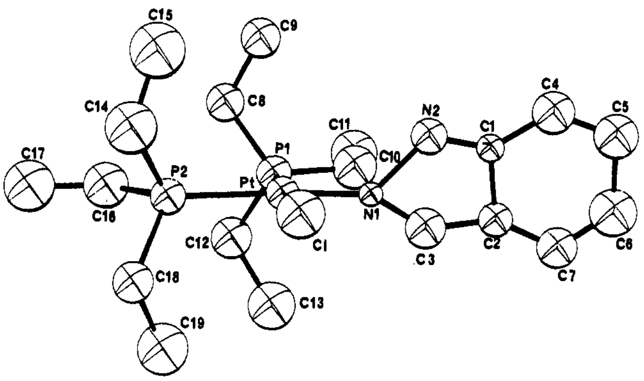

Figure 3. Molecular structure of *cis*-$[PtCl(PEt_3)_2(INN)][BF_4]\cdot(CH_3)_2CO$ (cation only).

Results

While cleavage of the chloro-bridged dimeric platinum(II) dication $Pt_2Cl_2(PEt_3)_4{}^{2+}$ proceeded readily with L = MTMP (eq 2), giving the white, air-stable product **1** in good yield, no

$$[M_2Cl_2(PEt_3)_4][BF_4]_2 + 2L = 2\,cis\text{-}[MCl(PEt_3)_2L][BF_4] \qquad (2)$$

similar reaction occurred where M = Pd. This is surprising since as a synthetic route eq 2 is generally equally applicable for M = Pd as for M = Pt, but it may be related to other observations consistent with poor coordinating behavior for MTMP. Thus although the carbonyl derivatives $M(CO)_5L$ (M = Cr, W) can be formed in high yield[8] when L = pzH, (3,5-DMP), etc., the corresponding complex for L = MTMP cannot be successfully purified. Likewise we have been unable to obtain a product of this type when L = bis(trifluoromethyl)pyrazole, and indeed, with the latter, reaction according

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[4] Other crystallographic programs used on a UNIVAC 1110 computer include ORTEP (thermal ellipsoid drawings, by C. K. Johnson) and BPL (least-squares planes, by W. E. Hunter).

[5] D. T. Cromer and B. Mann, *Acta Crystallogr., Sect. A*, **A24**, 321 (1968).

[6] "International Tables for X-ray Crystallography", Vol. 3, Kynoch Press, Birmingham England, 1962.

[7] D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).

[8] A. D. Garnovskii, N. E. Kolobova, O. A. Osipov, K. N. Anisimov, I. B. Zlotina, G. K. Mitina, and Yu. V. Kolodyazhnyi, *Zh. Obshch. Khim.*, **42**, 929 (1972).

Table I. Crystal Data and Summary of Intensity Data Collection and Structure Refinement

	$[PtCl(PEt_3)_2(MTMP)][BF_4]$	$[PtCl(PEt_3)_2(INN)][BF_4]\cdot(CH_3)_2CO$
mol wt	703.0	729.8
space group	$P\bar{1}$	$P\bar{1}$
cell dimens		
a, Å	8.977 (3)	9.074 (3)
b, Å	10.018 (4)	10.214 (4)
c, Å	15.893 (5)	17.161 (6)
α, deg	88.27 (2)	88.08 (2)
β, deg	83.88 (2)	81.16 (2)
γ, deg	72.22 (2)	73.46 (2)
cell vol, $Å^3$	1353.3	1506.5
molecules/unit cell	2	2
ρ(calcd), g cm^{-3}	1.72	1.61
μ(calcd), cm^{-1}	52.04	46.83
radiation	Mo Kα	Mo Kα
max crystal dimens, mm	0.10 × 0.30 × 0.40	0.05 × 0.30 × 0.45
scan width	0.80 + 0.20 tan θ	0.90 + 0.20 tan θ
std reflctns	400, 020, 004	400, 050, 008
decay of stds	±2%	^{a}
reflctns measd	3344	2212
2θ range, deg	44	36
reflctns obsd	2762	2030
no. of parameters varied	260	153
GOF	0.89	6.89
R	0.067	0.127
R_w	0.077	0.131

[a] Intensity lost steadily during data collection.

Table II. Fractional Atomic Coordinates for *cis*-$[PtCl(PEt_3)_2(MTMP)][BF_4]$

atom	x/a	y/b	z/c
Pt	0.21581 (9)	0.28681 (9)	0.22851 (5)
Cl	0.0065 (7)	0.2492 (8)	0.1649 (5)
P(1)	0.4108 (7)	0.3404 (6)	0.2861 (4)
P(2)	0.2087 (6)	0.0988 (5)	0.3098 (4)
F(1)	0.343 (2)	0.223 (2)	0.034 (1)
F(2)	0.490 (2)	0.345 (2)	0.020 (2)
F(3)	0.332 (3)	0.364 (3)	−0.067 (1)
N(1)	0.193 (2)	0.439 (3)	0.146 (1)
N(2)	0.081 (2)	0.582 (2)	0.163 (1)
C(1)	0.062 (3)	0.666 (2)	0.094 (2)
C(2)	0.159 (3)	0.589 (3)	0.027 (2)
C(3)	0.230 (2)	0.462 (2)	0.062 (1)
C(4)	−0.055 (3)	0.819 (3)	0.104 (2)
C(5)	0.343 (3)	0.353 (3)	0.016 (2)
C(6)	0.449 (3)	0.494 (2)	0.235 (2)
C(7)	0.592 (3)	0.529 (3)	0.270 (2)
C(8)	0.606 (3)	0.197 (3)	0.276 (2)
C(9)	0.652 (3)	0.158 (3)	0.185 (3)
C(10)	0.379 (4)	0.377 (3)	0.396 (2)
C(11)	0.250 (5)	0.494 (4)	0.416 (3)
C(12)	0.227 (3)	−0.053 (3)	0.243 (2)
C(13)	0.370 (4)	−0.091 (3)	0.178 (2)
C(14)	0.013 (3)	0.126 (2)	0.365 (1)
C(15)	−0.048 (3)	0.258 (3)	0.413 (2)
C(16)	0.343 (3)	0.037 (3)	0.391 (2)
C(17)	0.326 (3)	−0.095 (3)	0.442 (2)
B	0.826 (5)	0.774 (5)	0.353 (2)
F(4)	0.905 (3)	0.638 (3)	0.313 (2)
F(5)	0.727 (3)	0.834 (3)	0.297 (2)
F(6)	0.763 (4)	0.745 (3)	0.429 (2)
F(7)	0.944 (4)	0.809 (4)	0.350 (2)

to eq 2 fails to occur even when M = Pt. We suggest that the electron-withdrawing capacity of the CF_3 group(s) reduces the pyrazole donor ability to a point at which for MTMP the Pd–N interaction is not sufficiently strong to bring about complexation as in eq 2, which is promoted energetically for M = Pt through formation of a product having a stronger M–N bond. The INN analogue of **1**, **2**, was prepared according to eq 2 and was crystallized as the acetone monosolvate

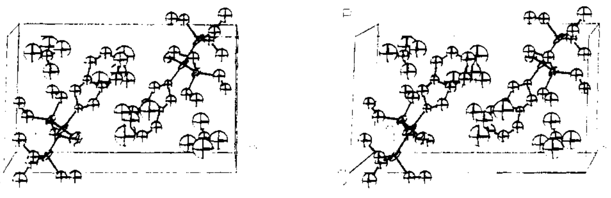

Figure 4. Crystal packing arrangement for *cis*-$[PtCl(PEt_3)_2(INN)][BF_4]\cdot(CH_3)_2CO$.

Table III. Selected Bond Lengths (Å) and Angles (deg) for *cis*-$[PtCl(PEt_3)_2(MTMP)][BF_4]$

Pt–Cl	2.357 (5)	Pt–P(1)	2.266 (5)
Pt–P(2)	2.265 (5)	Pt–N(1)	1.95 (3)
Cl–Pt–P(1)	175.6 (2)	Cl–Pt–P(2)	85.7 (2)
P(1)–Pt–P(2)	98.5 (2)	Cl–Pt–N(1)	83.2 (5)
P(1)–Pt–N(1)	92.7 (5)	P(2)–Pt–N(1)	168.8 (5)

Table IV. Fractional Atomic Coordinates for *cis*-$[PtCl(PEt_3)_2(INN)][BF_4]\cdot(CH_3)_2CO$

atom	x/a	y/b	z/c
Pt	0.1175 (2)	0.2974 (2)	0.2429 (1)
Cl	−0.111 (1)	0.267 (1)	0.3094 (7)
P(1)	0.339 (1)	0.337 (1)	0.1820 (6)
P(2)	0.136 (1)	0.103 (1)	0.1763 (6)
N(1)	0.067 (3)	0.459 (3)	0.311 (2)
N(2)	−0.031 (4)	0.600 (3)	0.228 (2)
C(1)	−0.052 (4)	0.684 (3)	0.350 (2)
C(2)	0.049 (5)	0.619 (4)	0.411 (2)
C(3)	0.097 (5)	0.482 (4)	0.373 (3)
C(4)	−0.146 (5)	0.822 (5)	0.364 (3)
C(5)	−0.141 (5)	0.891 (4)	0.428 (3)
C(6)	−0.046 (7)	0.834 (6)	0.490 (3)
C(7)	0.053 (6)	0.679 (5)	0.471 (3)
C(8)	0.354 (6)	0.361 (5)	0.078 (3)
C(9)	0.225 (5)	0.478 (4)	0.048 (2)
C(10)	0.357 (5)	0.503 (4)	0.225 (3)
C(11)	0.521 (6)	0.527 (6)	0.178 (3)
C(12)	0.519 (5)	0.208 (5)	0.195 (3)
C(13)	0.527 (5)	0.161 (5)	0.283 (3)
C(14)	−0.040 (5)	0.122 (4)	0.127 (2)
C(15)	−0.067 (6)	0.246 (5)	0.066 (3)
C(16)	0.298 (5)	0.029 (5)	0.103 (3)
C(17)	0.290 (7)	−0.098 (6)	0.056 (3)
C(18)	0.117 (5)	−0.049 (4)	0.243 (2)
C(19)	0.256 (5)	−0.069 (5)	0.299 (3)
B	0.7581	0.7784	0.1415
F(1)	0.653 (5)	0.839 (4)	0.212 (2)
F(2)	0.826 (4)	0.648 (4)	0.157 (2)
F(3)	0.698 (6)	0.805 (5)	0.079 (3)
F(4)	0.862 (6)	0.843 (6)	0.147 (3)
O	0.655 (5)	0.602 (5)	0.507 (3)
C(20)	0.557 (6)	0.674 (6)	0.466 (3)
C(21)	0.551 (8)	0.603 (7)	0.386 (4)
C(22)	0.453 (9)	0.809 (8)	0.496 (4)

Table V. Selected Bond Lengths (Å) and Angles (deg) for *cis*-$[PtCl(PEt_3)_2(INN)][BF_4]\cdot(CH_3)_2CO$ •

Pt–Cl	2.31 (1)	Pt–P(1)	2.26 (1)
Pt–P(2)	2.28 (1)	Pt–N(1)	1.96 (3)
Cl–Pt–P(1)	177.0 (4)	Cl–Pt–P(2)	85.0 (4)
P(1)–Pt–P(2)	98.0 (4)	Cl–Pt–N(1)	84.7 (8)
P(1)–Pt–N(1)	92.3 (8)	P(2)–Pt–N(1)	169.7 (8)

3. The bis(pyrazolyl) and -(indazolyl) platinum(II) complexes **4** and **5** were obtained in a manner identical with that reported previously for related azole derivatives.[9]

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(9) G. Minghetti, G. Banditelli, and F. Bonati, *J. Chem. Soc., Dalton Trans.*, 1851 (1979).

(10) G. W. Bushnell, K. R. Dixon, and M. A. Khan, *Can. J. Chem.*, **52**, 1367 (1974).

(11) G. W. Bushnell, K. R. Dixon, and M. A. Khan, *Can. J. Chem.*, **56**, 450 (1978).

Table VI. Comparison of Distances in $[PtCl(PEt_3)_2L]$ Cations

L	Pt-P,[a] Å	Pt-N, Å	Pt-Cl, Å	confign	θ, deg	ref
phenanthroline	2.239 (7), 2.241 (6)	2.137 (19)	2.361 (6)	cis	97.5	10
napthyridine	2.254 (4), 2.252 (4)	2.08	2.366 (4)	cis	92.0	11
phthalazine	2.269 (8), 2.252 (8)	2.08 (3)	2.354 (9)	cis	100.0	12
3-(trifluoromethyl)-5-methylpyrazole	2.265 (5), 2.266 (5)	1.95 (3)	2.357 (5)	cis	93.0	this study
indazole	2.28 (1), 2.26 (1)	1.96 (3)	2.31 (1)	cis	83.9	this study
$NH{=}NC_6H_4F$-*p*	2.320 (6)	1.973 (7)	2.291 (2)	trans		13
$NH_2NHC_6H_4F$-*p*	2.328 (2)	2.081 (7)	2.303 (2)	trans		13

[a] For cis compounds the first distance corresponds to the phosphine trans to L.

Crystal and Molecular Structures of 1 and 3. Molecular structures and crystal-packing arrangements are illustrated in Figures 1–4, and crystal data are collected in Table I. In terms of the isomerism represented by A and B in eq 1 it is clear that in the solid state complex **1** is a (3-(trifluoromethyl)-5-methylpyrazole)platinum(II) derivative while the indazole molecule in **3** is bound through N^2, i.e., coordination of INN as expected and not 2*H*-INN. The cis geometry for the cation is also confirmed in each case.

Atomic coordinates and bond lengths and bond angles are listed in Tables II and III for **1** and Tables IV and V for **3**, respectively, and a comparison of important distances with those determined elsewhere for related platinum compounds is represented in Table VI. As for these related compounds, there is no evidence for bidentate coordination, with the Pt–N^1 separation >3.0 Å in each structure.

For complex **1** the bond angles around the metal atom show the expected sterically induced deviations from 90 and 180°, with P(1)–Pt–P(2) enlarged to 98.5 (2)° and Cl–Pt–N(1) and Cl–Pt–P(2) narrowed to 83.5 (5) and 85.7 (2)°, respectively. Results of mean-planes calculations show variation within the platinum square plane of only 0.03 Å with the pyrazole ring planar to within 0.01 Å, but the Pt atom lies 0.3 Å out of the pyrazole plane. The angle between the two planes of 93° is similar to that occurring in all related compounds (Table VI). The interatomic distances in the heterocycle fall into a narrow range (1.36–1.39 Å) except for the N(1)–N(2) single bond at 1.49 (3) Å. The only short nonbonding contact is N(2)–F(4), which at 2.69 (3) Å represents the same kind of interionic interaction identified previously.[2a]

The esd's for complex **3** are greater than those for **1** due to the refinement difficulties commented on earlier, which may have arisen through slow loss of acetone solvent molecules from the crystal during x-ray data collection. This precludes meaningful discussion of the bond lengths in the heterocycle, but in contrast with the case for **1** least-squares plane calculations place the metal atom only 0.09 Å out of the indazole plane, the latter being planar within 0.07 Å with the Pt environment planar to 0.01 Å.

NMR Spectra. The ^{13}C NMR spectrum of the ligand MTMP recorded at 62.89 MHz is illustrated in Figure 5. It consists of three singlet resonances, with two others split through coupling to the three equivalent fluorine nuclei into binomial quartets. These data can thus be assigned unambiguously as follows (δ to high frequency vs. Me_4Si): 10.13 s (CH_3); 102.88 s (CH); 121.63 q, ^1J(C–F) = 268 Hz (CF_3); 141.62 s (C-CH_3); 142.89 q, ^2J(C–F) = 37 Hz (C-CF_3). The ^{19}F NMR spectrum consisted of a single line under all conditions, the chemical shift for which was found to be strongly solvent and temperature dependent (δ downfield vs. external $CFCl_3$): in $CDCl_3$, −41.21; in acetone-d_6, −61.58; Me_2SO-d_6, −51.87. The ^1H NMR spectrum ($CDCl_3$ solution) showed δ 6.35 s (4-proton) and 2.30 s (CH_3).

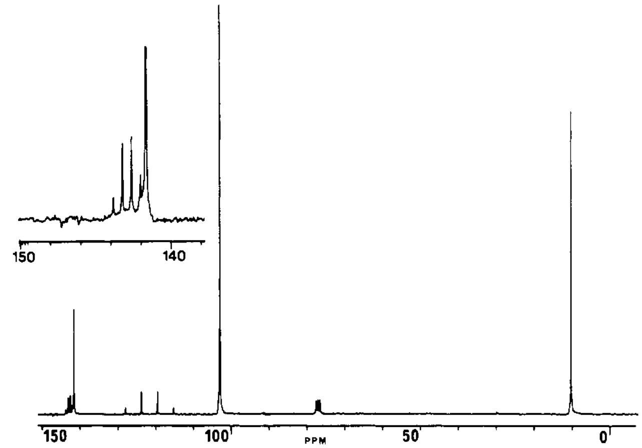


Figure 5. ^{13}C NMR spectrum of MTMP at 62.89 MHz in $CDCl_3$. The inset shows an expansion of the 140–150-ppm range.

Table VII. $^{31}P\{^1H\}$ NMR Data[a]

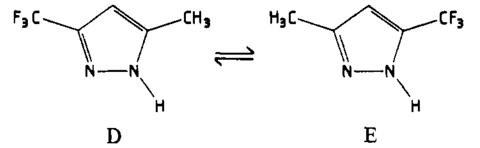
compd	$\delta(P_A)$	$\delta(P_B)$	$^1J(Pt\text{-}P_A)$	$^1J(Pt\text{-}P_B)$	$^2J(P\text{-}P)$
1	−132.9	−134.5	3433	3356	20
2	−133.4	−132.2	3429	3229	19
4	−138.5		3018		
5	−136.6		3002		

[a] δ values are positive downfield vs. $P(OMe)_3$; J values are in Hz. For **1** and **2** P_A is trans to Cl and P_B trans to N.

The platinum complexes **1**, **2**, **4**, and **5** were characterized in solution (CH_2Cl_2) initially by ^{31}P NMR spectroscopy. Data with assignments are presented in Table VII. The structure of complex **4** in solution was further examined with use of ^{13}C NMR, and the spectrum measured in $CDCl_3$ at 62.89 MHz is shown in Figure 6. Resonances centered at δ 8.31 and 15.41 (vs. Me_4Si) are due to phosphine methyl and methylene carbons, respectively, the former having $^3J(^{195}Pt\text{–}C)$ = 23 Hz and the latter splitting into a multiplet envelope by ^1J(P–C), $^2J(^{195}Pt\text{–}C)$, and ^3J(P–C). Signals assigned to pyrazolyl CH_3 and C-CF_3 are centered at 123.33 and 142.2 with ^2J(C–F) = 267 and 35 Hz, respectively. The ^{19}F resonances have no unexpected features indicative of the presence of more than one isomer for any of the compounds.

Discussion

Tautomeric exchange in MTMP as represented by eq 3 does



D E

(3)

not appear to have been established experimentally, and no structure determination directed toward distinguishing whether the molecule exists as D or E has been attempted in crystalline or gaseous states. The present NMR data suggest that, if an equilibrium exists in solution, one isomer overwhelmingly

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(12) G. W. Bushnell and K. R. Dixon, *Can. J. Chem.*, **56**, 878 (1978).

(13) S. D. Ittel and J. A. Ibers, *J. Am. Chem. Soc.*, **96**, 4804 (1974); *Inorg. Chem.*, **14**, 636 (1975).

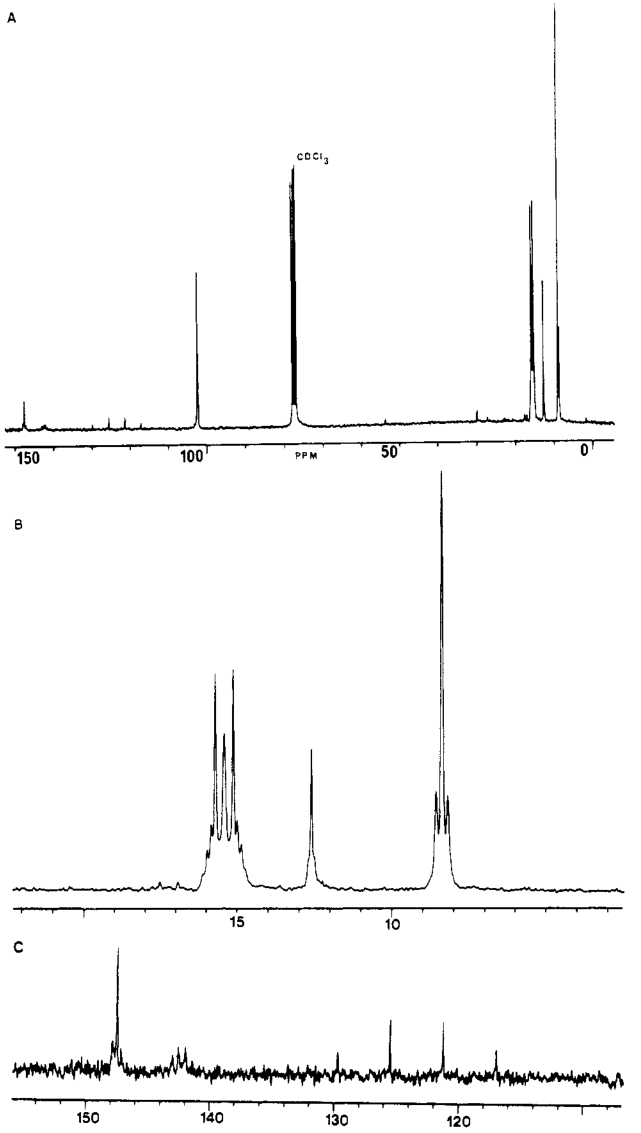


Figure 6. ^{13}C NMR spectrum of *cis*-$Pt(PEt_3)_2(C_5H_4F_3N_2)_2$ in $CDCl_3$ at 62.89 MHz: (A) full spectrum; (B) expansion of the 5–20-ppm range; (C) expansion of the 110–150-ppm range.

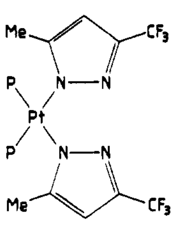
predominates or exchange is very rapid (single ^{19}F resonance). This is further supported by the fact that all resonances in ^1H or ^{13}C (Figure 5) NMR spectra show no discernible broadening and contain no unaccountable signals; on the assumption that the more basic N atom will be protonated, we tentatively propose that the isomer for which assignment of the ^{13}C NMR spectrum has been presented is that with configuration D. If this conclusion is correct, it offers a rationale for the observed coordination behavior: (a) through N^2 in the cationic complexes as established crystallographically; (b) through N^1 for the pyrazolide anion of D, indicated by the NMR data for complex **4** as discussed below. Thus the X-ray studies show that, in terms of the isomerism represented by A and B of eq 1, in the solid state complex **1** is a (3-(trifluoromethyl)-5-methylpyrazole)platinum(II) derivative, while as expected the indazole molecule in **3** is bound through N^2. The cis geometry indicated by the ^2J(P–P) values (Table VII) is confirmed for each cation.

The two structures described here correlate well with those of other members of the *cis*-$[PtCl(PEt_3)_2L]^+$ series as indicated in Table VI. Comparison with the trans structures provides a good illustration of the so-called "trans influence" in d^8 square-planar systems: thus the Pt–P bonds are longer, with the Pt–Cl distances being shorter in the *trans*-$[PtCl(PEt_3)_2L]^+$ cations. The Pt–N bond lengths of 1.95 (3) and 1.96 (3) Å in complexes **1** and **3** are rather short in relation to those determined for the other cis cations and are substantially so compared[2a] with Pd–N = 2.10 (2) Å in *cis*-$[PdCl(PEt_3)_2(3,5\text{-DMP})]^+$ (**6**) (DMP = dimethylpyrazole). This observation may be related to the nonfluxional character of the Pt(DMP) cations, a difference from Pd analogues we consider may be partly due to an increase in M–N bond strength between M = Pd and M = Pt; the latter coupled with the shortening of the M–N bond may imply more effective back-donation from the Pt atom into ligand π orbitals. Accordingly, the NMR data reported here show no evidence for stereochemically nonrigid character for **1** or **2**.

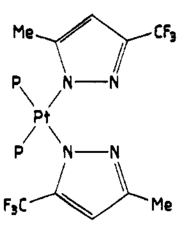
It is interesting that the MTMP ligand coordinates to Pt with the sterically more demanding substituent (CF_3) closest to the metal center; this effect is presumably responsible for the dislocation (0.3 Å) of the Pt atom out of the plane of the ring system. In contrast, in **3** the corresponding deviation is very much smaller (<0.1 Å), implying substantially less steric influence than the pyrazole ligands in **1** or **6**, although indazole has previously been referred to as a bulky ligand in the context of azole coordination.[14] The origin of the preference of Pt for coordination to N(1) may well be related to the formation of a strong F···H–N(2) intermolecular hydrogen bond. The H atom could not be located, but the F···N separation of 2.69 (3) Å is indicative of the interaction.

Comparison of the bond lengths in coordinated MTMP in **1** with those in 3,5-DMP in **6** reveals that N(1)–C(3) has lengthened from 1.319 (7) Å in the latter to 1.38 (3) Å. Furthermore, in **1** the C(1)–C(2) = 1.39 (3) Å and C(2)–C(3) = 1.37 (2) Å distances are significantly closer than in **6**: 1.35 (1) and 1.393 (9) Å, respectively. There is also a dramatic lengthening of the N–N distance, from 1.355 (9) Å in **6** to 1.49 (3) Å in **1**. Taken together, these observations are consistent with a considerably greater degree of bond delocalization in the coordinated MTMP ligand than for 3,5-DMP; this may result from the combined effect of the electron-withdrawing character of the CF_3 group attached to C^3 and inductive electron release from the CH_3 group on the opposite side of the heterocycle. The close N(2)–F(4) contact (2.69 (3) Å) in complex **1** parallels exactly the situation found[2a] in **6**, where the analogous distance was 2.79 (1) Å, and is again attributed to interionic hydrogen-bonding, F(4)···H–N(2), confirming the presence of a proton bound to N(2) in **1**.

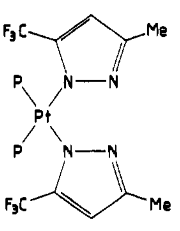
Formation of complex **4** through the reaction of *cis*-$PtCl_2(PEt_3)_2$ with the pyrazolide anion follows a route established earlier by us and others.[9,15] The magnitude of ^1J(Pt-P) (Table VII) establishes that **4** has a cis geometry, for which three isomeric arrangements are possible, F–H. The



F



G



H

singlet unsplit ^{31}P resonance rules out the unsymmetrical configuration G and moreover strongly indicates that only one isomer is present in solution (i.e., F or H). In this context, in the ^{13}C NMR spectrum of **4** we note the following: (i) spin coupling to Pt-195 (33.8%, $I = {}^1/_2$) is observed for C-CH_3, CH_3, and CH but not for C-CF_3 or CF_3; (ii) the chemical shift

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of C-CH_3 moves significantly to high frequency on complexation (from 141.6 to 147.5 ppm) while that for C-CF_3 is virtually unchanged (from 142.9 to 142.2 ppm). We suggest that these data clearly point to F as the structure for **4**, i.e., the isomer in which the methyl substituent in each heterocyclic unit is closest to Pt.

Conclusion

The observations reported herein offer an interesting insight into the chemistry of MTMP. It seems likely that the molecule exists predominantly, if not exclusively, as 3-(trifluoromethyl)-5-methylpyrazole in solution, i.e., with the proton attached to the nitrogen center nearest to the inductive influence of the methyl group and furthest from the electron-withdrawing trifluoromethyl substituent, and that accordingly its coordination properties as a neutral species will center around ligation through N^2. The corresponding pyrazolyl (pyrazolide) anion complexes via M–N bond formation to the other nitrogen atom N^1, which is the more basic atom when it becomes available through deprotonation.

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Registry No. 1, 84049-91-2; **2**, 84056-83-7; **3**, 84056-84-8; **4**, 84049-92-3; **5**, 84049-93-4; $[Pt_2Cl_2(PEt_3)_4][BF_4]_2$, 19394-82-2; *cis*-$PtCl_2(PEt_3)_2$, 15692-07-6.

Supplementary Material Available: Listings of thermal parameters, least-squares planes, and observed and calculated structure factors for **1** and **3** (35 pages). Ordering information is given on any current masthead page.

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Kinetics of the Oxidation of Chromium(II) by Hydrogen Peroxide: Flash-Photolytic and Stopped-Flow Studies Based on Radical-Trapping Reactions

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Thermally stable organochromium complexes such as $CrCHCl_2^{2+}$ and $CrCH_2OCH_3^{2+}$ undergo homolytic Cr–C bond cleavage upon irradiation with unfiltered light from xenon flash lamps: $CrR^{2+} \xrightarrow{h\nu} Cr^{2+} + R\cdot$. This enables determination of the rate constant k_1 for the reaction $Cr^{2+} + H_2O_2 \rightarrow CrOH^{2+} + \cdot OH$, because this is the rate-limiting step in a sequence of reactions. The hydroxyl radicals react very rapidly with organic and inorganic solutes to yield radicals that in turn react rapidly with Cr^{2+}, producing intensely colored chromium complexes. The formation of these species was monitored spectrophotometrically. Some experiments were also done by the stopped-flow technique using solutions of Cr^{2+} and H_2O_2 in the presence of an organic solute or KI. The two techniques yielded identical results. In aqueous solution at 25 °C and 1.0 M ionic strength ($HClO_4 + LiClO_4$), with methanol, ethanol, 2-propanol, dimethyl ether, diethyl ether, dimethyl sulfoxide, and potassium iodide as solutes, the value of the rate constant k_1 is $(7.06 \pm 0.04) \times 10^4\ M^{-1}\ s^{-1}$.

Introduction

The reaction of H_2O_2 with Cr^{2+} has been studied extensively.[1,2] It was shown that the reaction proceeds mainly via a one-electron-transfer mechanism[1a,b] according to eq 1–3.

$$Cr^{2+} + H_2O_2 \xrightarrow{k_1} CrOH^{2+} + \cdot OH \qquad (1)$$

$$Cr^{2+} + \cdot OH \xrightarrow{\text{fast}} CrOH^{2+} \qquad (2)$$

$$2Cr^{2+} + H_2O_2 = 2CrOH^{2+} \qquad (3)$$

This particular reaction was briefly addressed as part of a study[2] of the kinetics of reactions between hydrogen peroxide and metal complexes. Side reactions complicated the kinetics when H_2O_2 was used in excess over Cr^{2+}; thus the reported rate constant $k_1 = (2.8 \pm 0.7) \times 10^4\ M^{-1}\ s^{-1}$ was obtained with Cr^{2+} in excess. (As we point out later, the value reported in the literature[2] was calculated incorrectly and is too low by a factor of 2.) The rather large error is due to small absorbance changes in the stopped-flow experiments and to high reaction rates.

Owing to the formation of the OH radicals in reaction 1, the Cr^{2+}–H_2O_2 reaction proved to have a valuable synthetic utility in the preparation of various cationic organochromium complexes,[3-5] reactions 4 and 5, where R, R^1, R^2 = alkyl or hydrogen.

$$HCR^1R^2OR + \cdot OH \rightarrow \cdot CR^1R^2OR + H_2O \qquad (4)$$

$$\cdot CR^1R^2OR + Cr^{2+} \rightarrow CrCR^1R^2OR^{2+} \qquad (5)$$

The organochromium complexes produced have characteristic strong absorption bands at ~400 and ~300 nm with molar absorptivities ($M^{-1}\ cm^{-1}$) ranging from several hundred at the first maximum to ~2500 at the second.[3-5] This property of the organochromium complexes greatly enhances the absorbance change in the overall reaction, thus permitting an accurate measurement of the rate constant for reaction 1. In addition to large absorbance changes, this approach has the advantage in that the scavenging of the OH radicals (eq 4) eliminates side reactions and either reagent can be used in excess. This enabled us to generate low concentrations of Cr^{2+} ($\sim 3 \times 10^{-5}$ M) flash photolytically from the thermally stable organochromium complexes $CrCHCl_2^{2+}$ and $CrCH_2OCH_3^{2+}$. Handling of low concentrations of Cr^{2+} in the stopped-flow apparatus could thus be avoided.

Results and Discussion

Flash-Photolytic Experiments. When a solution of $\geq 1 \times 10^{-4}$ M $CrCHCl_2^{2+}$ is exposed to a 50-J flash, the absorbance

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