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Palladium(II) and Platinum(II) Complexes with Nucleobases and Nucleosides. Crystal Structure of *trans*-Bis(adeninato)bis(tri-*n*-butylphosphine)palladium(II)

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The synthesis and degradation of the dinuclear and tetranuclear complexes $[L(n\text{-}Bu_3P)MCl]_2$ and $[Cl_2(n\text{-}Bu_3P)M(L)M(P\text{-}n\text{-}Bu_3)Cl]_2$ [M = Pd(II), Pt(II)] with the anion of adenine (L) have been studied. A series of complexes *trans*-$(n\text{-}Bu_3P)_2PdL_2$ and $[L(n\text{-}Bu_3P)PdCl]_n$ with L = adeninate, cytosinate, guaninate, guanosinate, inosinate, theophyllinate, thyminate, uracilate, and uridinate, as well as adenosine-bridged complexes $Cl_2(n\text{-}Bu_3P)M$–adenosine–$M(P\text{-}n\text{-}Bu_3)Cl_2$ [M = Pd,Pt], have been synthesized. The spectroscopic data of the new complexes are reported. Crystals of *trans*-$(n\text{-}Bu_3P)_2Pd(\text{adeninate})_2{\cdot}4CH_3OH$ are triclinic (space group $P\bar{1}$) with the cell parameters a = 10.993 (2) Å, b = 11.945 (2) Å, c = 10.140 (2) Å, α = 105.36 (1)°, β = 91.80 (1)°, and γ = 93.16 (1)°. The structure was refined to $R_1 = 0.045$ and $R_2 = 0.051$. The X-ray structure determination shows that adeninate is coordinated via N(9) and that the purine rings are virtually orthogonal to the coordination plane P_2PdN_2. The colorless crystals are stabilized by hydrogen bonds between the oxygen atoms of the methanol molecules and N(3) and N(7) of adenine. Intermolecular hydrogen bonding is observed between the amino group $N(6)H_2$ and N″(1). Thus, with the exception of the metalated N(9) atom all of the adeninate N atoms are involved in hydrogen bonding.

As a result of the antitumor activity of some transition-metal complexes,[2] considerable interest has been shown in the design of model complexes which could mimic the interaction of metal ions with DNA.[2-4] A number of studies have established that the nucleobases are the preferred sites of attack by *cis*-diammine platinum(II) compounds.[2] As a continuation of our previous studies on the preparation and isolation of a number of metal complexes with nucleobases and nucleosides,[5] we report new palladium and platinum complexes and reactions thereof. An X-ray structure determination of a palladium(II) complex with anionic adenine has been carried out.

Preparative Results

We have particularly studied the reactions of chloro-bridged $[Pd(PBu_3)Cl_2]_2$ with adenine. One of our aims in this chemistry was to prepare palladium and platinum compounds which contain complementary nucleobases in cis or trans positions, $[L_2M(\text{nucleobase})(\text{nucleobase}')]$. Such compounds could be considered as a simple model for a cross-linking system where the metal bridges two DNA strands. Cross-linking of DNA strands is one of the likely mechanisms for the antineoplastic properties of Pt(II) complexes.[2]

For this purpose the tetranuclear and binuclear palladium adeninate complexes Ia and IIa[5] have been reacted with phosphines in order to produce monomeric compounds of the type $(R_3P)_2PdClL$ (L = adeninate) which could be further treated with another anionic nucleobase L′ to give the desired complexes $(R_3P)_2PdLL'$.

The synthesis and degradation of monomeric, dimeric, and tetranuclear adeninate palladium complexes are summarized in Scheme I, where L is the anion of adenine.

By reaction of the chloro-bridged complex $[n\text{-}Bu_3PPdCl_2]_2$ with an excess of potassium adeninate all chloro ligands could be replaced by adeninate giving V.[5] V was also obtained from IIa with adeninate. An analogous complex both with terminal and bridging anionic heterocycles has previously been described with triazolate.[6]

The reaction of IIa with phosphine yields the monomeric bis(adeninate) complex IVa and *trans*-$Cl_2Pd(PBu_3)_2$. Obviously the expected complex $Cl(L)Pd(PBu_3)_2$ (III) is not stable and disproportionates to IVa and $Cl_2Pd(PBu_3)_2$.

Similarly, the tetranuclear platinum compound $[Pt_2(PBu_3)_2LCl_3]_2$ (Ib) prepared by the same method as described for Ia[5] reacts with phosphines to give dimeric $L(Bu_3P)PtCl_2Pt(PBu_3)L$ (IIb) and *cis*-$Cl_2Pt(PBu_3)_2$. The trans and cis structures of $Cl_2Pd(PBu_3)_2$ and $Cl_2Pt(PBu_3)_2$, respectively, are established by their infrared spectra. The trans complex shows only one (350 cm^{-1}) ν(M–Cl) stretching band, while the cis compound shows two ν(M–Cl) stretching bands (280, 305 cm^{-1}).

Disproportionation has also been observed when IIa was reacted with tributylphosphine in the presence of the second nucleobase thyminate (L′) to give IVa and IVf.

Further monomeric and chloro-bridged complexes of the type $L_2Pd(PBu_3)_2$ and $[L(Cl)PdPBu_3]_n$ have been obtained by nucleophilic substitution of chloride by an anionic nucleobase L^-:

$$\textit{trans}\text{-}Cl_2Pd(PBu_3)_2 \xrightarrow[-2Cl^-]{2L^-} \underset{\text{IV}}{\textit{trans}\text{-}L_2Pd(PBu_3)_2}$$

$$[Cl_2Pd(PBu_3)]_2 \xrightarrow[Cl^-]{L^-} \underset{\text{II}}{[L(Bu_3P)PdCl]_n}$$

complex	L	complex	L
IIa IVa	adeninate	IIf IVf	thyminate
IVb	theophillinate	IVg	uracilate
IIc IVc	guanosinate	IVh	uridinate
IId IVd	inosinate	IVi	guaninate
IIe IVe	cytosinate		

0020-1669/79/1318-0176$01.00/0

Scheme I

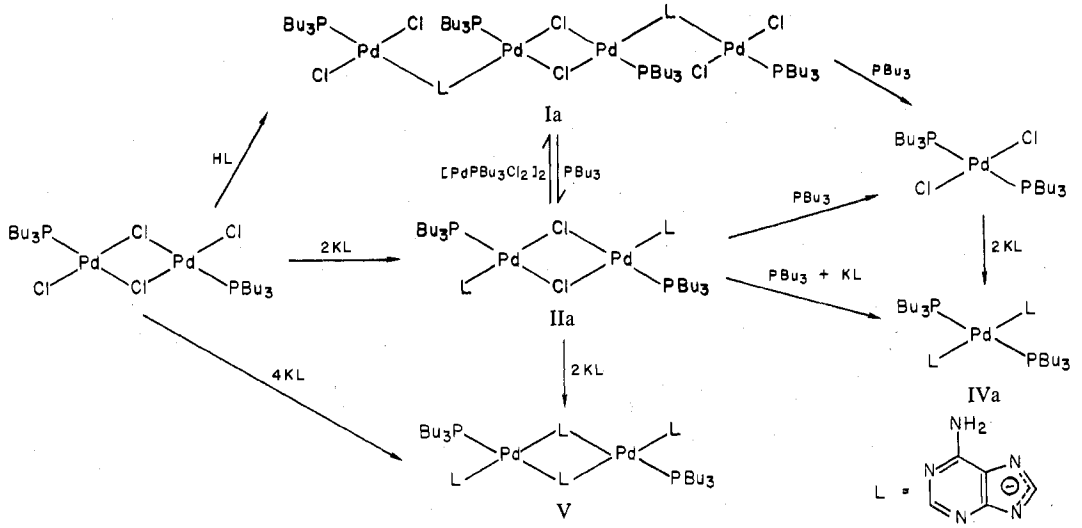
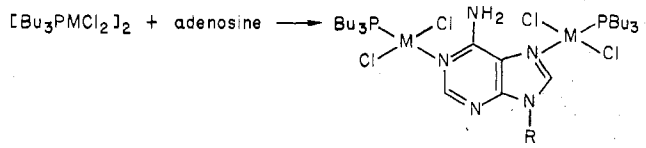


Table II. Proton Chemical Shifts Relative to Me_4Si (δ, in ppm) and Coordination Shifts (Δ,[a] in ppm) for Me_2SO-d_6 Solutions of Free and Coordinated Adenine and Adenosine

compd	C(2)H		C(8)H		$C(6)NH_2$	C(1')H
	δ	Δ	δ	Δ		
adenine (LH)	8.26		8.18		7.20	
Ia	8.48	+0.22	7.96	−0.22	7.70	
IIa	8.23	−0.03	7.58	−0.60	6.93	
IVa	8.18	−0.08	7.65	−0.53	6.65	
$[W(CO)_5L]^-$ [b]	8.16	−0.10	7.53	−0.65	6.67	
$(n\text{-}Bu_3P)_2Rh(L)CO$ [c]	8.05	−0.21	7.40	−0.78	6.43	
$(n\text{-}Bu_3P)_2PtL_2$ [c]	8.00	−0.26	7.35	−0.83	6.42	
V	8.53, 8.22	+0.27, −0.04	8.07, 7.60	−0.11, −0.58	7.43, 6.70	
potassium adeninate	7.83	−0.43	7.52	−0.66		
adenosine	8.30		8.42		7.38	5.98[d]
2',3'-*O*-isopropylidene-adenosine	8.25		8.42		7.42	6.23[d]
VIa	8.37	+0.07	8.72	+0.30	7.70	6.00[f]
VIb[e]	8.54	+0.24	8.64	+0.22	8.30, 7.65	5.87[f]
VIc	8.43	+0.18	8.80	+0.38	8.27	6.10[f]

[a] $\Delta = \delta_{complex} - \delta_{LH}$. [b] Reference 3. [c] N. Kottmair, Thesis, University of Munich, 1977. [d] $J_H = 6$ Hz. [e] Bruker, 270 MHz, $CDCl_3$. [f] Coupling not resolved.

Adenosine was found to react with $[(Bu_3P)MCl_2]_2$ (M = Pd, Pt) to afford the adenosine-bridged complex VI:



VIa, M = Pd,
R = ribosyl
b, M = Pt,
R = ribosyl
c, M = Pt,
R = 2',3'-*O*-isopropylidene ribosyl

The palladium complex VIa was described earlier.[5] Recently an analogous 9-methyladenine-bridged platinum complex where the phosphine ligand is substituted by dialkyl sulfoxide was reported[7] and it was shown by an X-ray structure determination that the platinum atoms are coordinated via N(1) *and* N(7).

Spectroscopic Data

Characteristic IR data of the adeninate complexes are tabulated in Table I and are available as supplementary material.

The intense absorptions of IVb–i at 1630 cm^{-1}, which are attributed to the ν(C=O) mode, indicate that in no case does the exocyclic oxygen atom take part in coordination.[5]

From the $\nu_s(NH_2)$ and $\nu_{as}(NH_2)$ bands of the 0.01 M solution spectra of IVa, a coordination of adeninate via the amino group can be excluded. As with 9-ethyladenine,[8] the shift of the $\nu(NH_2)$ vibrations and the appearance of new bands at lower wavenumbers in more concentrated $CHCl_3$ solutions of IVa (0.1 M) are due to association through hydrogen bonds.

For Ia no such concentration effect could be observed (Figure 1). Since the observed relation between $\nu_{as}(NH_2)$ and $\nu_s(NH_2)$ does not agree with the calculated ratio $\nu_s/\nu_{as} = 0.97$[9] that was found for the free NH_2 group in IVa (in 0.01 M solution), the two protons of the exocyclic amino group in Ia experience different environments. The low-frequency band at 3308 cm^{-1} is indicative of an intramolecular H-bonded ν(NH) stretching mode, while the high-frequency band at 3470 cm^{-1} corresponds to nonbonded NH.[7] The high value of 3470 cm^{-1} also excludes $C(6)NH_2$–metal bonding.

The $\delta(NH_2)$ band of the adeninate complexes appears at 1620–1635 cm^{-1} (in $CHCl_3$) and has been found to be very intense. The position of this band is sensitive to hydrogen bonding. In the solid spectrum of IVa (in KBr) the $\delta(NH_2)$ absorption is shifted to higher wavenumbers. Whereas from the IR spectra it cannot be decided which endocyclic nitrogen atom coordinates to the metal, the ^1H NMR spectra clearly

Table III. ^{13}C Chemical Shifts of Adenine and Adenosine and Their Metal Complexes (Values Given are ppm from Me_4Si)

compd	C(2)	C(4)	C(5)	C(6)	C(8)	C(1′)	C(2′)	C(3′)	C(4′)	C(5′)	solvent
adenine[a]	152.5	151.4	117.6	155.4	139.4						Me_2SO-d_6
potassium adeninate	152.7	154.5	120.6	159.6	149.9						D_2O
Ia	150.7	153.8	118.1	153.8	150.3						$CDCl_3$
Ib	154.2	155.5	118.3	155.5	154.2						THF/CH_3OD
IIa	152.2	156.1	121.0	156.6	149.4						THF/CH_3OD
adenosine[b]	152.6	149.3	119.6	156.3	140.2	88.2	73.8	70.9	86.1	61.9	Me_2SO-d_6
VIa	154.9	148.6	119.4	155.7	144.6	91.3	75.7	71.7	87.6	62.8	THF/CH_3OD

[a] Reference 10. [b] Reference 11.

Table IV. ^{31}P Chemical Shifts Relative to 85% Phosphoric Acid (δ, in ppm), Coordination Shifts (Δ,[a] in ppm), and ^{195}Pt-^{31}P Coupling Constants (J, in Hz) of Adeninate and Adenosine Complexes

compd	δ	Δ	$^1J_{Pt-P}$	solvent
$[n\text{-}Bu_3PPdCl_2]_2$	−38.4	−71.1		THF
VIa	−29.5	−62.2		THF
Ia	−25.9	−58.6		THF
IIa	−12.1	−44.8		THF/MeOH
$[n\text{-}Bu_3PPtCl_2]$	−1.6	−34.3	3861	THF
VIb	+6.1	−26.6	3468	THF
VIc	+6.5	−26.2	3454	MeOH
Ib	+7.5	−25.2	*b*	THF

[a] $\Delta = \delta_{complex} - \delta_{PBu_3}$; $\delta_{PBu_3} = 32.7$. [b] Ib was not enough soluble to detect J_{Pt-P}.

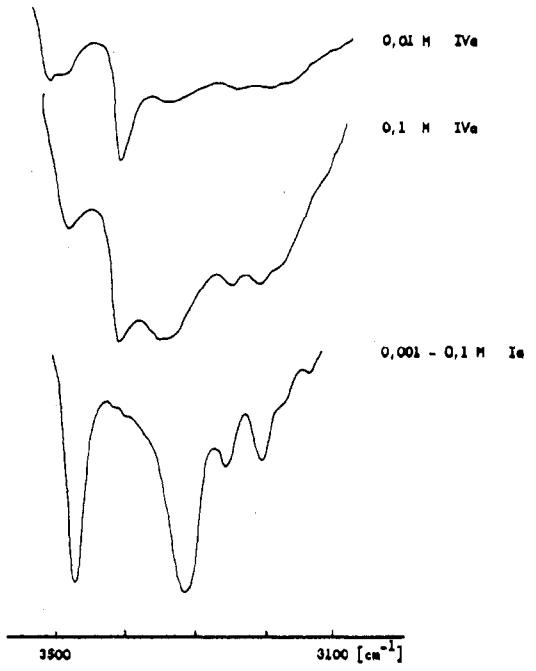


Figure 1. $\nu(NH_2)$ bands of IVa and Ia in chloroform solutions.

indicate coordination via the imidazole ring at N(7) or N(9) since the coordination shift (compared to that for neutral adenine) for C(8)H is found to be larger than that for C(2)H (Table II). The proton NMR signals of the adeninate complexes have been assigned according to the literature.[10] In the adeninate-bridged complex Ia, a positive coordination shift for the C(2)H is observed. The proton NMR signals of V support the presence of both terminal and bridging adeninate ligands (Table II). As expected in the adenosine-bridged compound VIa, C(8)H is less shielded. In the 270-MHz spectrum of VIb the two NH_2 protons are nonequivalent. This has also been found for cytosine–mercury and –gold complexes[11] and can be attributed to restricted rotation around the C–NH_2 bond caused by coordination to the metal via the adjacent N(1) atom.

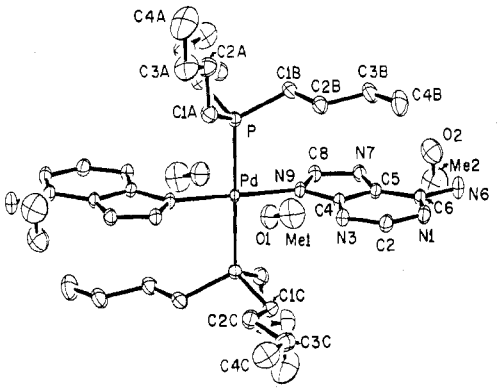


Figure 2. Structure and labeling system for *trans*-$(n\text{-}Bu_3P)_2$Pd-(adeninate)$_2$·$4CH_3OH$ (20% thermal ellipsoids). Hydrogens have been omitted for clarity.

Table V. Interatomic Distances (Å)

Pd-P(1)	2.349 (1)	C(8)-N(9)	1.359 (5)
Pd-N(9)	2.015 (3)	C(5)-C(4)	1.378 (5)
P(1)-C(1A)	1.827 (5)	C(1A)-C(2A)	1.510 (7)
P(1)-C(1B)	1.827 (4)	C(2A)-C(3A)	1.503 (8)
P(1)-C(1C)	1.821 (5)	C(3A)-C(4A)	1.446 (11)
C(2)-N(1)	1.332 (6)	C(1B)-C(2B)	1.519 (6)
C(6)-N(1)	1.351 (6)	C(2B)-C(3B)	1.509 (6)
C(2)-N(3)	1.326 (5)	C(3B)-C(4B)	1.498 (8)
C(4)-N(3)	1.366 (5)	C(1C)-C(2C)	1.507 (7)
C(6)-N(6)	1.346 (5)	C(2C)-C(3C)	1.527 (7)
C(5)-C(6)	1.412 (5)	C(3C)-C(4C)	1.475 (9)
C(5)-N(7)	1.373 (5)	Me(1)-O(1)	1.350 (9)
C(8)-N(7)	1.319 (5)	Me(2)-O(2)	1.353 (10)
C(4)-N(9)	1.356 (5)		

Table VI. Intramolecular Angles (deg)

P(1)-Pd-N(9)	87.71 (9)	C(4)-C(5)-C(6)	117.4 (4)
P(1)-Pd-N(9)	92.29 (9)	N(1)-C(6)-N(6)	119.5 (4)
Pd-P(1)-C(1A)	112.8 (2)	C(5)-C(6)-N(1)	117.7 (4)
Pd-P(1)-C(1B)	116.5 (2)	C(5)-C(6)-N(6)	122.7 (4)
Pd-P(1)-C(1C)	111.5 (2)	N(9)-C(8)-N(7)	115.0 (4)
C(2)-N(1)-C(6)	118.8 (3)	C(1A)-P(1)-C(1B)	106.1 (2)
C(4)-N(3)-C(2)	111.2 (4)	C(1A)-P(1)-C(1C)	104.5 (2)
C(8)-N(7)-C(5)	103.0 (3)	C(1B)-P(1)-C(1C)	104.5 (2)
C(8)-N(9)-C(4)	104.3 (3)	P(1)-C(1A)-C(2A)	118.8 (4)
Pd-N(9)-C(4)	127.6 (3)	P(1)-C(1B)-C(2B)	114.8 (3)
Pd-N(9)-C(8)	128.1 (2)	P(1)-C(1C)-C(2C)	115.2 (3)
N(3)-C(2)-N(1)	129.3 (4)	C(1A)-C(2A)-C(3A)	113.8 (5)
N(9)-C(4)-N(3)	126.8 (3)	C(2A)-C(3A)-C(4A)	115.6 (8)
C(5)-C(4)-N(3)	125.6 (3)	C(1B)-C(2B)-C(3B)	113.2 (4)
N(9)-C(4)-C(5)	107.6 (4)	C(2B)-C(3B)-C(4B)	114.2 (5)
N(7)-C(5)-C(4)	110.1 (3)	C(1C)-C(2C)-C(3C)	112.2 (4)
N(7)-C(5)-C(6)	132.5 (4)	C(2C)-C(3C)-C(4C)	113.2 (5)

The ^{13}C NMR spectra of adenine,[12] of adenosine,[13] and of some nucleobase and nucleoside complexes[14] have been reported. A tentative assignment for the ^{13}C NMR signals of potassium adeninate, Ia, Ib, IIa, and VIa is given in Table III. The ^{31}P chemical shifts of some complexes are listed in Table IV. As with chloro complexes, the coordination shift for Pd complexes is larger than for corresponding Pt compounds. The large Pt–P coupling constants for VIb and VIc which have also

Table VIII. Molar Conductance [$cm^2/(\Omega$ mol)] of Some Nucleobase and Nucleoside Complexes

compd	Λ, $cm^2/(\Omega$ mol)	solvent	compd	Λ, $cm^2/(\Omega$ mol)	solvent
Ia	0.2	acetone	IVa	0.7×10^{-3}	MeOH
Ib	3.5	acetone	V	13.1	MeOH
IIa	0.9	acetone	VIa	0.3	acetone
IIb	11.4	MeOH	VIb	0.2	acetone

been found in mixed *trans*-(phosphine)(amine)platinum complexes[15] support the proposed structure of an adenosine bridge between two platinum atoms.

Molecular Structure of *trans*-Bis(adeninato)bis(tri-*n*-butylphosphine)palladium(II)

A view of IVa with its four associated methanol molecules of solvation is shown in Figure 2. The bond lengths and angles with estimated deviations from the full inverse matrix are given in Tables V and VI. The molecule possesses crystallographic site symmetry $\bar{1}$ with the palladium constrained to lie on the inversion center. The palladium atom is coordinated to two trans tri(*n*-butyl)phosphine ligands and two trans monodentate adeninate ligands which are coordinated through N(9). Coordination through N(9), the most basic of the four available nitrogen atoms on the adenine anion, is well documented.[4] The resulting coordination about palladium is square-planar with the Pd–P(1) distance 2.349 (1) Å and the Pd–N(9) distance 2.015 (3) Å, which is that expected for a normal Pd–N single-bond distance. In bis(histamino)palladium dichloride[16] and bis(6-mercapto-9-benzylpurine)palladium(II)[17] and the Pd–N distances are 2.029 and 2.047 Å, respectively. A distance of 2.005 Å is reported in bis(5-phenyltetrazolato)bis(triphenylphosphine)palladium(II).[6] The Pd–P distance of 2.351 Å reported in the latter compound also agrees well with that found in this study. The P(1)–Pd–N(9) angle is 87.71 (9)°. The bond lengths and angles within the adenine ligand are remarkably similar ($<3\sigma$) to those reported in adenosine[18] and a compound in which an adenine anion is coordinated to cobalt.[19] The adenine ring is planar, with the maximum deviation of an atom out of the plane of 0.022 Å at C(5). As might be expected, the adenine ligands minimize steric repulsions with the bulky tri(*n*-butyl)phosphine ligands by lying perpendicular to the plane defined by the palladium, phosphorus, and nitrogen atoms, the angle between the adenine ligand and this plane being 92.0°. The *n*-butyl groups are also planar to within 0.005 Å for group A, 0.03 Å for group B, and 0.02 Å for group C, and it is interesting to note that steric repulsions for these planes are minimized by orienting perpendicular to the adenine plane for group A (91°) and perpendicular to the palladium, phosphorus, and nitrogen coordination plane for groups B and C (90 and 96°, respectively). The orientation of the coordinated ligands is further integrated with the four solvated methanol molecules via strong hydrogen bonding. The methanol(1) molecule fits neatly into a pocket defined by N(3), C(2C), and C(8)′ with the O(1)–N(3) distance 2.914 (5) Å. This also places atom O(1) in a pseudooctahedral environment about the palladium although the Pd–O(1) distance of 3.462 (4) Å is not indicative of an interaction. The second methanol donates its OH proton to N(7), the next most basic nitrogen in the adenine ligand, while the methanol oxygen is simultaneously hydrogen bonded through one of the protons on N(6). The O(2)–N(7) distance, 2.774 (5) Å, is noticeably shorter than the other packing distances. The O(2)–N(6) distance is 2.972 (6) Å. Interestingly, atom O(2) is exactly coplanar with the adenine plane. The remaining nitrogen atom N(1) is involved with *inter*-molecular hydrogen bonds from the second proton on N(6) in a molecule related by $(1 - x, -y, 1 - z)$, with N(1)–N(6)″ = 2.975 (5) Å. Thus, with the exception of the metalated N(9) atom, all of the adenine N atoms participate in hydrogen bonding.

Table IX. Positional Parameters for *trans*-$(n\text{-}Bu_4P)_2Pd(adeninate)_2 \cdot 4CH_3OH$ ($\times 10^4$) and Isotropic Thermal Parameters

atom	*x*	*y*	*z*	B_{iso}, Å^2
Pd	0	0	0	
P(1)	−1320.3 (9)	−849.3 (9)	1292.8 (11)	
N(9)	1382 (3)	−694 (3)	794 (3)	
C(8)	1867 (4)	−1732 (4)	263 (4)	
N(7)	2781 (3)	−1960 (3)	1004 (4)	
C(5)	2904 (3)	−993 (3)	2103 (4)	
C(4)	2048 (3)	−222 (3)	1979 (4)	
N(3)	1917 (3)	832 (3)	2886 (3)	
C(2)	2743 (4)	1042 (4)	3918 (4)	
N(1)	3621 (3)	383 (3)	4153 (4)	
C(6)	3738 (4)	−656 (4)	3245 (4)	
N(6)	4637 (3)	−1320 (4)	3452 (4)	
C(1A)	−996 (4)	−2347 (4)	1222 (5)	
C(2A)	−1775 (5)	−3007 (5)	2002 (6)	
C(3A)	−1441 (7)	−4238 (6)	1837 (8)	
C(4A)	−2179 (10)	−4906 (8)	2551 (11)	
C(1B)	−2950 (4)	−881 (4)	862 (5)	
C(2B)	−3399 (4)	−1808 (4)	−426 (5)	
C(3B)	−4614 (4)	−1579 (5)	−1002 (6)	
C(4B)	−5125 (6)	−2529 (6)	−2204 (7)	
C(1C)	−1161 (4)	−85 (4)	3105 (4)	
C(2C)	−1641 (5)	1111 (4)	3482 (5)	
C(3C)	−1246 (5)	1795 (5)	4943 (5)	
C(4C)	−1767 (8)	2940 (6)	5366 (8)	
O(1)	576 (4)	2701 (3)	2313 (4)	
Me(1)	1159 (8)	3689 (7)	3097 (9)	
O(2)	4523 (4)	−3508 (4)	1205 (5)	
Me(2)	4002 (9)	−4452 (8)	1519 (10)	
HO1	950	2084	2444	8.0
HMe1	782	4302	2960	8.0
HMe1	1935	3726	2854	8.0
HMe1	1134	3689	3978	8.0
HO2	3945	−3016	1145	8.0
HMe2	4584	−4941	1579	8.0
HMe2	3442	−4810	858	8.0
HMe2	3651	−4225	2325	8.0
H4B	−5847	−2334	−2493	8.0
H4C	−1504	3300	6233	8.0
H4A	−1902	−5633	2383	8.0
H4A	−2109	−4567	3448	8.0
H4A	−2954	−4960	2238	8.0
H4B	−4604	−2625	−2885	8.0
H4B	−5234	−3194	−1954	8.0
H4C	−2585	2840	5322	8.0
H4C	−1526	3371	4808	8.0
H1B	−3139	−177	782	8.0
H1B	−3377	−972	1573	8.0
H2B	−3453	−2508	−247	8.0
H2B	−2840	−1863	−1066	8.0
H3B	−4546	−904	−1240	8.0
H3B	−5155	−1454	−339	8.0
H1C	−373	−37	3393	8.0
H1C	−1528	−524	3595	8.0
H2C	−2461	1048	3388	8.0
H2C	−1376	1508	2893	8.0
H3C	−427	1890	5025	8.0
H3C	−1459	1373	5525	8.0
H1A1	−203	−2372	1460	8.0
H1A1	−985	−2763	341	8.0
H2A	−2566	−3009	1736	8.0
H2A	−1729	−2624	2897	8.0
H3A	−647	−4238	2091	8.0
H3A	−1453	−4614	938	8.0
H4	1580	−2222	−536	8.0
H9	2707	1728	4551	8.0
H6	5070	−957	4232	8.0
H6	4605	−1978	2765	8.0

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer 325 spectrometer. Spectra of solids were obtained as KBr pellets; solution spectra were

Table X. Anisotropic Thermal Parameters for *trans*-(n-Bu_3P)$_2$Pd(adeninate)$_2$·$4CH_3OH$[a]

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pd	2.27 (2)	3.20 (2)	2.71 (2)	0.15 (1)	−0.61 (1)	1.03 (2)
P(1)	3.19 (5)	4.27 (6)	3.98 (5)	0.16 (4)	−0.18 (4)	1.73 (4)
N(9)	3.0 (1)	4.1 (2)	3.5 (1)	0.4 (1)	−0.9 (1)	1.4 (1)
C(8)	3.4 (2)	4.3 (2)	4.0 (2)	0.5 (1)	−0.5 (1)	1.4 (2)
N(7)	3.4 (2)	4.7 (2)	4.8 (2)	0.7 (1)	−0.5 (1)	1.9 (1)
C(5)	3.0 (2)	4.2 (2)	3.7 (2)	0.2 (1)	−0.7 (1)	1.7 (2)
C(4)	2.8 (2)	4.3 (2)	3.4 (2)	0.1 (1)	−0.5 (1)	1.7 (2)
N(3)	3.7 (2)	4.6 (2)	3.8 (2)	0.2 (1)	−0.8 (1)	1.1 (1)
C(2)	4.5 (2)	5.3 (2)	3.9 (2)	0.0 (2)	−0.7 (2)	1.3 (2)
N(1)	4.1 (2)	5.6 (2)	4.4 (2)	0.0 (1)	−1.5 (1)	1.8 (2)
C(6)	3.3 (2)	5.6 (2)	4.6 (2)	0.2 (2)	−0.7 (2)	2.7 (2)
N(6)	4.6 (2)	6.7 (2)	5.8 (2)	0.9 (2)	−2.4 (2)	1.8 (2)
C(1A)	4.6 (2)	5.2 (2)	6.1 (3)	0.5 (2)	0.1 (2)	2.5 (2)
C(2A)	6.6 (3)	6.6 (3)	6.9 (3)	−0.9 (2)	−0.1 (2)	3.5 (2)
C(3A)	11.2 (5)	6.8 (4)	12.5 (5)	−1.2 (3)	−0.9 (4)	6.3 (4)
C(4A)	18.2 (9)	9.0 (5)	15.5 (7)	−3.5 (5)	−3.7 (6)	7.1 (5)
C(1B)	3.4 (2)	4.9 (2)	5.6 (2)	0.0 (2)	0.1 (2)	1.6 (2)
C(2B)	3.8 (2)	4.9 (2)	6.0 (2)	−0.3 (2)	−0.3 (2)	2.2 (2)
C(3B)	3.6 (2)	6.6 (3)	7.7 (3)	−0.5 (2)	−0.7 (2)	2.8 (2)
C(4B)	6.1 (3)	8.4 (4)	9.9 (4)	−1.7 (3)	−3.1 (3)	3.4 (3)
C(1C)	4.6 (2)	6.1 (3)	4.0 (2)	−0.1 (2)	0.1 (2)	2.0 (2)
C(2C)	5.6 (3)	5.9 (3)	5.0 (2)	0.7 (2)	−0.1 (2)	1.5 (2)
C(3C)	7.4 (3)	6.5 (3)	5.1 (3)	−0.6 (2)	0.5 (2)	0.9 (2)
C(4C)	13.1 (6)	7.5 (4)	9.0 (4)	0.1 (4)	0.4 (4)	0.1 (3)
O(1)	7.8 (2)	5.8 (2)	7.9 (2)	1.1 (2)	−1.0 (2)	1.6 (2)
Me(1)	11.9 (6)	7.3 (4)	12.8 (6)	2.1 (4)	−0.5 (5)	1.2 (4)
O(2)	7.9 (3)	7.1 (2)	11.4 (3)	2.9 (2)	0.2 (2)	3.1 (2)
Me(2)	13.7 (7)	8.5 (5)	13.0 (6)	3.0 (5)	0.2 (5)	2.9 (5)

[a] Temperature factors are in the form $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

solvent compensated. ^1H, ^{31}P, and ^{13}C NMR spectra were obtained using Varian A60, Varian HA 100, and Bruker HFX-90 spectrometers. Decomposition points were determined using a Büchi melting point apparatus and were uncorrected. Starting materials *trans*-Pd(PBu_3)$_2Cl_2$[20] and [n-Bu_3PMCl_2]$_2$ (M = Pd,[21] Pt[22]) were prepared according to literature methods; *trans*-Pd(PBu_3)$_2Cl_2$ and [n-Bu_3PMCl_2]$_2$ (M = Pd, Pt) were recrystallized from pentane and acetone, respectively. The nucleobases, nucleosides, and dimethyl-d_6 sulfoxide were purchased commercially and used without further purification. All solvents were distilled before use.

Preparation of Compounds. Bis(adeninato)hexachlorotetrakis(tri-*n*-butylphosphine)tetrapalladium(II) [Ia]. Method A. Adenine, 270 mg (2 mmol), was dissolved in 40 mL of ethylene glycol monomethyl ether, and 760 mg (1 mmol) of [n-Bu_3PPdCl_2]$_2$ was added to the solution. After 1–2 days of stirring at 20 °C, the solvent was removed in vacuo, and the resulting yellow residue was taken up in THF. The insoluble adenine hydrochloride was filtered off and the filtrate was evaporated to a volume of 3 mL. The yellow product, which tends to oil, was obtained by careful addition of petroleum ether (yield 80%).

Method B. IIa, 200 mg (0.21 mmol), and 160 mg (0.21 mmol) of [n-Bu_3PPdCl_2]$_2$ were stirred in 10 mL of chloroform for 2 days at 20 °C. After 2 mL of *n*-octane was added to the yellow solution, the $CHCl_3$ was removed by blowing a stream of nitrogen through the solution. The yellow precipitate was collected, washed with petroleum ether, and dried in vacuo (yield 90%).

Bis(adeninato)hexachlorotetrakis(tri-*n*-butylphosphine)tetraplatinum(II) [Ib]. This compound was prepared as described above for Ia, method A, using 270 mg of adenine and 940 mg of [n-Bu_3PPtCl_2]$_2$.

Reaction of Ia with PBu_3. Tributylphosphine, 0.03 mL (0.12 mmol), was added with stirring to a solution of 100 mg (0.06 mmol) of Ia in 5 mL of THF. After 1 day, the solvent was removed in vacuo and the resulting solid was taken up in pentane. The insoluble IIa was filtered off. The yellow filtrate was partly evaporated and allowed to stand for a few days at −20 °C. The yellow crystals of *trans*-(Bu_3P)$_2PdCl_2$ were collected and dried in vacuo (yield 60 mg (0.1 mmol)). IIa was recrystallized from 0.5 mL of methanol at −20 °C; yield 40 mg (0.04 mmol) (66%).

Reaction of Ib with PBu_3. Tributylphosphine, 0.06 mL (0.22 mmol), was added with stirring to a solution of 230 mg (0.11 mmol) of Ib in 5 mL of THF. After 2 days, the solvent was removed. The resulting solid was suspended in pentane and allowed to stand for several days. The insoluble compound IIb was filtered off (yield 0.09 mmol) and the filtrate, containing *cis*-Pt(PBu_3)$_2Cl_2$ was evaporated to dryness. IIb and Pt(PBu_3)$_2Cl_2$ were recrystallized from ethanol.

Reaction of IIa with PBu_3. Tributylphosphine, 303 mg (1.5 mmol), was carefully added with stirring to a solution of 707 mg (0.75 mmol) of IIa in 10 mL of THF. After 3 days, the colorless precipitate (IVa) was filtered off. The filtrate was evaporated to dryness and the oily, yellow residue was placed upon a cellulose column. Elution with pentane yielded *trans*-Pd(PBu_3)$_2Cl_2$, which was freed from impurities of tributylphosphine oxide at 80 °C (10^{-3} torr).

Bis(adeninato)dichlorobis(tri-*n*-butylphosphine)dipalladium(II) [IIa]. Adenine, 270 mg (2 mmol), and 115 mg (2 mmol) of potassium hydroxide in 30 mL of methanol were stirred together with 760 mg (1 mmol) of [n-Bu_3PPdCl_2]$_2$ for 2 h at 20 °C. The clear, yellow mixture was allowed to stand for 4 days at −20 °C during which period the product crystallized out of the solution. The yellow crystals were collected, washed with cold methanol, and dried in vacuo (yield 50%). To improve the yield, the filtrate was evaporated to dryness and the residue washed with water and cold methanol (total yield 90%).

Bis(adeninato)dichlorobis(tri-*n*-butylphosphine)diplatinum(II) [IIb]. Adenine, 300 mg (2.25 mmol), and 168 mg (3 mmol) of potassium hydroxide were dissolved in 150 mL of hot methanol. The cooled and filtered solution was stirred with 937 mg (1 mmol) of [n-Bu_3PtCl_2]$_2$ for 2 days. The methanol was removed in vacuo; the colorless product was washed with water and dried over P_2O_5 in vacuo (yield 90%).

Preparation of Compounds IIc–IIf. General Procedure. Procedure A. One millimole of ligand, 1 mmol of potassium hydroxide, and 0.5 mmol of [n-Bu_3PPdCl_2]$_2$ were dissolved in 30 mL of ethylene glycol monomethyl ether and stirred for 2–3 days. The solvent was removed under vacuum at 40 °C and the resultant residue extracted with acetone. After the filtrate was concentrated, the pale yellow product was precipitated by adding pentane. Yields were about 80%.

Procedure B. A solution of 0.5 mmol of [n-Bu_3PPdCl_2]$_2$ in 25 mL of methanol was added to a solution of 1 mmol of ligand and 1 mmol of potassium hydroxide in 5 mL of water. After 3 days, the methanol was distilled off and the resulting precipitate was collected on a glass frit. The yellow solid was washed with water and dried over a P_2O_5 in vacuo. Yields were 70–80%.

***trans*-Bis(adeninato)bis(tri-*n*-butylphosphine)palladium(II) [IVa]. Method A.** A solution of 582 mg (1 mmol) of *trans*-(n-Bu_3P)$_2PdCl_2$ in 20 mL of THF was added with stirring to a solution of 1.35 g (10 mmol) of adenine and 560 mg (10 mmol) of potassium hydroxide in 20 mL of water. After 12 h, the initial yellow mixture was colorless and the precipitate was collected and washed with diluted aqueous KOH and water and recrystallized from methanol. If precipitation

did not occur, THF was evaporated until the solid began to separate. The colorless transparent crystals are only stable with methanol. On standing in air, the crystals lose methanol and turn immediately into a white powder (yield 60%).

Method B. IIa, 700 mg (0.73 mmol), and 300 mg (1.5 mmol) of tri-*n*-butylphosphine were added with stirring to a filtered solution of potassium adeninate which was prepared by dissolving 270 mg (2 mmol) of adenine and 112 mg (2 mmol) of potassium hydroxide in 50 mL of boiling methanol. The yellow reaction mixture became colorless after stirring for 2–3 days. The colorless precipitate was collected, washed with 2 N KOH and water, and recrystallized from methanol (yield 75%).

Preparations of Compounds IVb–IVi. General Procedure. A solution of 3 mmol of the nucleobase or the nucleoside and 3 mmol of KOH in 10 mL of water was added to a solution of 1 mmol of *trans*-$(n\text{-}Bu_3P)_2PdCl_2$ in 20 mL of methanol. After the solution was stirred for 2 days, the methanol was evaporated. The resulting precipitate was collected, washed with water, and dried over P_2O_5 in vacuo (yield 80%). The nucleobase complexes are white whereas the nucleoside compounds are pale yellow.

Tetrakis(adeninato)bis(tributylphosphine)dipalladium(II) [V]. Method A. Adenine, 810 mg (6 mmol), and 340 mg (6 mmol) of potassium hydroxide were dissolved in 100 mL of hot methanol. After the solution was cooled to room temperature, 760 mg (1 mmol) of $[n\text{-}Bu_3PPdCl_2]_2$ was added to the filtered solution. The mixture was stirred for 2 days. The solvent was removed in vacuo. The resultant pale yellow residue was washed with water and dried over P_2O_5 in vacuo, giving a yield of 70%.

Method B. A solution of 478 mg (0.5 mmol) of IIa in 50 mL of methanol was added to a solution of 405 mg (3 mmol) of adenine and 168 mg (3 mmol) of potassium hydroxide in 100 mL of methanol. The mixture was stirred for 2 days at room temperature. The solvent was partly removed under vacuum and the pale yellow product was precipitated by adding aqueous 2 N potassium hydroxide. The product was collected on a glass frit, washed several times with water, and dried over P_2O_5 in vacuo (yield 80%).

(Adenosine)tetrachlorobis(tributylphosphine)dipalladium(II) and -diplatinum(II) [VIa and VIb]. Adenosine, 800 mg (3 mmol), and 0.5 mmol of $[n\text{-}Bu_3MCl_2]_2$ (M = Pd, Pt) in 40 mL of ethylene glycol monomethyl ether were stirred for 3 days at room temperature. The solvent was removed in vacuo at 60 °C and the residue extracted with 30 mL of ether. After filtrate was concentrated, the product was precipitated by adding pentane. The yellow complex was dried in vacuo for 8 h (yield 90%).

(2′,3′-*O*-Isopropylideneadenosine)tetrachlorobis(tributylphosphine)diplatinum(II) [VIc]. 2′,3′-*O*-isopropylideneadenosine, 307 mg (1 mmol), and 937 mg (1 mmol) of $[n\text{-}Bu_3PPtCl_2]_2$ in 5 mL of ether were stirred for 1–2 days at room temperature. The yellow, oily product was precipitated with pentane, washed with hot water, and dried over P_2O_5 in vacuo (yield 90%).

X-ray Structure Determination for *trans*-Bis(adeninato)bis(tri-*n*-butylphosphine)palladium(II) [IVa]. Colorless needles of IVa prepared according method B were obtained by slow evaporation of a methanol–water solution. The crystal chosen, a parallelepiped with dimensions 0.25 mm on each side, was wedged and sealed in a Lindemann glass capillary in the presence of mother liquor. The sample was placed on a Syntex $P\bar{1}$ autodiffractometer equipped with a graphite-monochromated Mo Kα source. After careful crystal and tube alignment, 15 diffraction maxima were measured and used to obtain cell parameters:[23] a = 10.993 (2) Å, b = 11.945 (2) Å, c = 10.140 (2) Å, α = 105.36 (1)°, β = 91.80 (1)°, γ = 93.16 (1)°, V = 1280.5 (4) Å^3. The triclinic Laue symmetry and associated lattice constants were verified by partial rotation photographs along each of the three reciprocal axes.

Intensity data were collected in the θ–2θ scan mode with the takeoff angle set to 4°. Variable scan rates were allowed from 2 to 24°/min with the total fixed background set to two-thirds of the scan time. A total of 5000 reflections were measured in the scan range $2° \leq 2\theta \leq 50°$. An examination of two standard reflections every 50 measurements showed no variation of intensity throughout the data collection. The data were treated[24] for Lorentz and polarization effects and merged to give 3674 reflections with $I > 2\sigma(I)$.[25] Effects of absorption were minimal (μ = 4.60 cm^{-1}) and were ignored. The calculated density for $PdP_2O_4N_{10}C_{38}H_{78}$ is 1.177 g/cm^3 (Z = 1). The density was not measured due to the extreme instability of the crystals when removed from the mother liquor.

The structure was solved from the standard Patterson method and refined[26] isotropically to R_1 = 0.091 and R_2 = 0.105.[27] After several cycles of anisotropic refinement including idealized coordinates for the hydrogen atoms (C–H, = O–H, = 0.90 Å) and anomalous dispersion for Pd and P, the R_1 and R_2 values were 0.045 and 0.051.[28] A difference map phased on the nonhydrogen atoms revealed all hydrogen atoms with the exception of one hydrogen on each methanol methyl group and two hydrogens on butyl group A. Both OH hydrogens appeared in anticipated positions and gave no indication of disorder. Attempts to refine the hydrogens, however, led to large shifts in the coordinates and further refinement varied only nonhydrogen atoms. The final full-matrix cycle converged to R_1 = 0.045 and R_2 = 0.051. The final data/parameter ratio was 14.7 and the standard deviation of an observation of unit weight was 1.16. The final positional and thermal parameters are given in Tables IX and X.

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Registry No. Ia, 67988-42-5; Ib, 67988-43-6; IIa, 68013-37-6; IIb, 67988-44-7; IIc, 68013-52-5; IId, 67988-45-8; IIe, 68070-48-4; IIf, 68070-47-3; IIg, 68070-49-5; IVa, 67921-65-7; IVb, 59053-65-5; IVc, 67921-66-8; IVd, 67921-67-9; IVe, 68070-45-1; IVf, 68070-44-0; IVg, 68070-46-2; IVh, 67938-26-5; IVi, 59372-54-2; V, 67988-46-9; VIa, 59368-76-2; VIb, 67921-68-0; VIc, 67921-69-1; *trans*-$(n\text{-}Bu_3P)_2PdCl_2$, 17523-47-6; *cis*-$Cl_2Pt(PBu_3)_2$, 15390-92-8; $[n\text{-}Bu_3PPdCl_2]_2$, 14882-49-6; $[n\text{-}Bu_3PPtCl_2]_2$, 15670-38-9.

Supplementary Material Available: Table I listing IR data, Table VII listing analytical data and decomposition points of the described complexes, and a listing of observed and calculated structure factor amplitudes (21 pages). Ordering information is given on any current masthead page.

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(25) The integrated intensity (I) was calculated according to the expression $I = [S - (B_1 + B_2)/B_R]T_R$, where S is the scan count, B_1 and B_2 are the background counts, B_R is the ratio of background time to scan time, and T_R is the 2θ scan rate in degrees per minute. The standard deviation of I was calculated as $\sigma(I) = T_R[S + (B_1 + B_2)/B_R^2 + \sigma(I)^2]^{1/2}$.
(26) All least-squares refinements were based on the minimization of $\sum w_i||F_o| - |F_c||^2$ with the individual weights $w_i = 1/\sigma(F_o)^2$.
(27) $R_1 = [\sum||F_o| - |F_c||/|F_o|] \times 100\%$ and $R_2 = [\sum w_i||F_o| - |F_c||^2/\sum w_i|F_o|^2]^{1/2} \times 100\%$.
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Diagnostic Features of Transition-Metal–SO_2 Coordination Geometries

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SO_2 complexes have been carefully examined in regard to possible correlations involving their physicochemical properties and SO_2 coordination geometries (coplanar MSO_2, pyramidal MSO_2, bridging MSO_2M, O,S-bonded SO_2, or ligand–SO_2 interaction). On a 1:1 basis, general correlations of geometry with SO infrared stretching frequencies, reversibility of SO_2 binding, and tendency of a complex to undergo the sulfato reaction can be made, but exceptions do exist. However, certain *combinations* of properties have been found to be diagnostic of specific geometries and appear to be useful criteria for identifying modes of SO_2 binding. The synthesis and properties of two new complexes, $Ir(SPh)(CO)(PPh_3)_2(SO_2)$ and $[RhCl(PPh_3)_2(SO_2)]_2$, are described in relation to the above correlations. These species as well as $RhCl(PPh_2Me)_3(SO_2)$ were found to react with atmospheric oxygen to form sulfates, which also were isolated and characterized.

Introduction

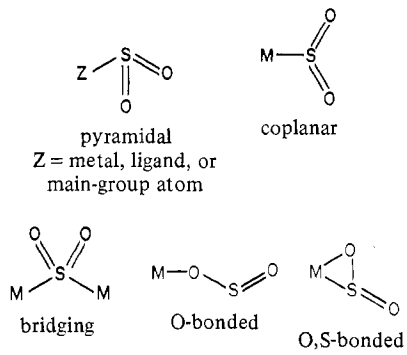
Few, if any, small molecules coordinate to a larger variety of substrates in a greater number of modes than sulfur dioxide. Excluding "insertion"-type structures,[1a] five different SO_2 coordination geometries have now been established by X-ray crystallography (Chart I). A complete listing of complexes possessing these structures is given in Table I. Of obvious interest is a means other than X-ray crystallography to determine which of these structural possibilities is most probable in a given transition-metal complex containing SO_2. In the past, efforts to correlate structure and physicochemical properties were primarily limited to the observation that compounds with pyramidal MSO_2 generally possessed a lower set of SO stretching frequencies than those with coplanar MSO_2.[1b] Also, in regard to the question of whether the SO_2 is S-bonded or O-bonded, a diagnostic based on Δ, the observed difference between the two SO stretching frequencies, has been proposed.[2] As part of an ongoing study of SO_2 complexes,[3-15] we have been closely scrutinizing complexes in regard to ν(SO), reversibility of SO_2 attachment, and reactivity with oxygen to form sulfates and have found that, in the majority of cases, correlations of structure with each of these properties can be made on a one-to-one basis. Occasional exceptions, even to the structure–infrared relation, do occur, which make structural predictions based on any one given property unreliable. However, certain *combinations* of properties have been found to be, without exception, diagnostic of specific coordination geometries and appear to be useful for identifying modes of SO_2 binding in newly synthesized complexes.

In the course of the above investigation, new SO_2 adducts have been synthesized and characterized also. The observed properties of these species will be discussed in relation to the proposed diagnostic features.

Experimental Section

All reactions except those requiring oxygen as a reactant were carried out in an atmosphere of dry nitrogen. Sulfur dioxide (Matheson, 99.98%), phosphines (Strem Chemicals), and other reagents were purchased commercially and used as received. $MCl(CO)(PPh_3)_2(SO_2)$ (M = Rh, Ir) and $RhCl(PPh_3)_3$ were synthesized according to methods described in *Inorganic Syntheses* (Vol.

Chart I



IX and X, respectively). $Ir(SPh)(CO)(PPh_3)_2$,[16] $RuCl_2(PPh_3)_2(SO_2)$,[17] $CpMn(CO)_2(SO_2)$[18] (Cp = η-C_5H_5), $[Ir(dppe)_2]Cl$[19] (dppe = $Ph_2PCH_2CH_2PPh_2$), $Ni(p_3)(SO_2)$[20] [p_3 = 1,1,1-tris(diphenylphosphinomethyl)ethane], $RhCl(PCy_3)_2(SO_2)$[21] (Cy = cyclohexyl), $Mo(CO)_3(phen)(\eta^2$-$SO_2)$[22] (phen = 1,10-phenanthroline), and $RhCl(PPh_2Me)_3(SO_2)$[23] were prepared according to literature methods. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Thermogravimetric curves and Nujol mull infrared spectra were recorded using Perkin-Elmer Models TGS-2 and 521, respectively.

Preparation of $RhCl(SO_4)(PPh_2Me)_3 \cdot {}^3/_4C_6H_6$. $RhCl(PPh_2Me)_3(SO_2)$ (0.35 g) was dissolved in 50 mL of warm benzene, and the solution was filtered and saturated with oxygen. A yellow-orange crystalline precipitate (0.13 g) formed upon allowing the loosely stoppered solution to stand for 3 days at room temperature. The precipitate was collected on a frit, washed with a small quantity of benzene and then pentane, and dried in air. Infrared and elemental analysis indicated that lattice benzene was present in the sulfate. Anal. Calcd for $C_{43.5}H_{43.5}P_3O_4SClRh$: C, 58.4; H, 4.9; P, 10.4; S, 3.6. Found: C, 58.3; H, 4.8; P, 10.0; S, 3.8.

Thermogravimetric analysis (2.5 °C/min heating rate) of $RhCl(SO)_4(PPh_2Me)_3 \cdot {}^3/_4C_6H_6$ indicated loss of benzene at 50–100 °C, loss of one phosphine at 150–225 °C, and further phosphine loss to 500 °C.

Preparation of $Ir(SPh)(CO)(PPh_3)_2(SO_2) \cdot C_7H_8$. $Ir(SPh)(CO)(PPh_3)_2$ was dissolved in toluene (~0.4 g/25 mL). The resulting yellow solution was treated with excess SO_2 gas, giving an immediate color change to deep red. The filtered solution was then reduced to

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