calculations on a group of osmium cluster carbonyls.[13] These calculations confirm the validity of the schematic energy level diagram, Figure 5, and provide quantitative information about the distribution of molecular orbital energy levels in these cluster species. While it is possible that there are transitions in the low-energy part of the visible spectrum that are associated purely with the metal cluster (M–M → M–M* transitions), the calculations on both Pt[1,3,5] and Os[13] cluster carbonyls provide strong support for assigning the main visible/UV bands to metal cluster carbonyl $2\pi^*$ transitions. In view of the quantitative features of the energy level diagrams for these clusters[13] and our experience with the platinum cluster carbonyls,[3,5,14] we suggest that the transitions between filled and empty M–M 5d levels, if they occur, should be associated with the background absorption shown in Figures 1–4 but that the two main peaks in the spectra involve carbonyl $2\pi^*$ levels. The observed absorption coefficients of these main peaks, which are typical of fully allowed electric dipole transitions, are consistent with this interpretation. A more refined interpretation of cluster spectroscopy must await further experiments; single-crystal measurements and/or MCD could be particularly helpful.

In summary, the optical absorption spectra of these high-nuclearity osmium cluster carbonyls show a strong parallel with those found and predicted for the dianions, $[Pt_3(CO)_6]_n^{2-}$.[3,5] This should not be surprising since both sets of compounds have metal cluster cores that are columnar rather than globular. The Os_{20} cluster for example can be thought of as having a metal core built up as a stack of five M_3 triangles with additional Os atoms bonded to the top and bottom layers (the central M_3 unit containing the heteroatom Hg)—see Figure 8d.

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Registry No. $[PPN]_2[Os_{10}C(CO)_{24}]$, 75117-74-7; $[PPN]_2[Os_{11}C(CO)_{27}]$, 110589-42-9; $[Os_{10}C(CO)_{24}I_2]$, 81181-60-4; $[PPN]_2[Os_{20}Hg(C)_2(CO)_{48}]$, 106466-56-2.

Contribution from the Dipartimento di Chimica
Inorganica e Struttura Molecolare, Università di Messina,
98100 Messina, Italy, and Christopher Ingold Laboratories,
University College London, London WC1H, England

Dissociative Substitution in Four-Coordinate Planar Platinum(II) Complexes. 3. Kinetics of the Displacement of Sulfur Donors from *cis*-Dimethylbis(dimethyl sulfoxide)- and *cis*-Dimethylbis(dimethyl sulfide)platinum(II) by Bidentate Ligands

Domenico Minniti,[†] Giuseppe Alibrandi,[†] Martin L. Tobe,[‡]
and Raffaello Romeo*[†]

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The usual mode of ligand substitution in four-coordinate planar d^8 metal complexes involves associative activation and considerable discrimination between the different nucleophiles.[1] The dissociative mode of activation is a rarity. A dissociative pathway has been characterized for the cis → trans isomerization of *cis*-$[Pt(PEt_3)_2(R)X]$ (where R is an alkyl or aryl group),[2,3] but in every case there is a more facile associatively activated pathway for ligand substitution.[4] Recently we showed that the displacement of dimethyl sulfoxide from *cis*-$[PtPh_2(Me_2SO)_2]$ by bidentate ligands in benzene solution occurred by a dissociatively activated pathway, with an intermediate that could discriminate between different nucleophiles[5] and have ruled out the alternative possibility that the sulfoxide, functioning temporarily as a bidentate, promotes this behavior by showing that *cis*-$[PtPh_2(Me_2S)_2]$ behaves in a similar way, albeit with an intermediate of much lower nucleophilic discrimination ability.[6] In both cases, stronger nucleophiles can also use a parallel associatively activated pathway.

In order to test the generality of the observation and to rule out the possibility that the dissociative mode of activation arises from some assistance from the ortho hydrogen of the phenyl group, we have extended our studies to the reactions

$$cis\text{-}[PtMe_2L_2] + L\text{-}L \rightarrow [PtMe_2(L\text{-}L)] + 2L$$

($L = Me_2SO$, Me_2S; L-L = a bidentate N, S, or P donor) and report the results in this paper.

Experimental Section

Preparation of Complexes. *cis*-Dimethylbis(dimethyl sulfoxide)platinum(II) was prepared by reacting *cis*-$[PtCl_2(Me_2SO)_2]$ with $SnMe_4$ in Me_2SO according to the method of Eaborn et al.[7]

cis-Dimethylbis(dimethyl sulfide)platinum(II) could not be isolated from solution and was prepared in situ by adding a sufficient excess (at least 50-fold) of dimethyl sulfide to a solution of the Me_2S-bridged dimer $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ in accordance with the method of Scott and Puddephatt.[8]

$[PtMe_2(L\text{-}L)]$. The syntheses of most of the complexes of this type that were postulated as reaction products have already been described in the literature. Displacement of the diolefin from $[PtMe_2(COD)]$ (COD = 1,5-cyclooctadiene) by L-L (L-L = 2,2′bipyridine (bpy),[9] 1,10-phenanthroline (phen),[9] 1,3-bis(diphenylphosphino)propane (dppp)[10] or of the sulfoxide from *cis*-$[PtMe_2(Me_2SO)_2]$ (L-L = bipyrimidine (bpym),[11] 1,2-bis(diphenylphosphino)ethane (dppe)[7]) has previously been described. The last method was also used to prepare the hitherto unknown complex where L-L = 1,2-bis(phenylthio) ethane (dpte). ^1H NMR ($CDCl_3$): δ(MePt) 0.789 (t, ^2J(PtH) = 86.36 Hz), $\delta(CH_2S)$ 2.91 (t, ^3J(PtH) = 18 Hz).

All complexes were characterized through elemental analysis, infrared spectroscopy, ^1H NMR spectroscopy and, where relevant, ^{31}P NMR and electronic spectroscopy. 1,2-Bis(phenylthio)ethane was prepared according to the literature method.[12] 1,10-Phenanthroline hydrate was dehydrated by heating under vacuum for 24 h at 80 °C, mp 117 °C. Other compounds were the best available commercial materials purified by recrystallization or distillation where necessary.

Infrared spectra were recorded as Nujol mulls on a Perkin-Elmer 783 spectrometer; ^1H and ^{31}P NMR spectra were recorded at 80 MHz on a Bruker WP 80 spectrometer using C_6D_6, $CDCl_3$, or $(CD_3)_2CO$ as solvent and tetramethylsilane and H_3PO_4 (externally), respectively, as standards.

Kinetics. Slower reactions were followed spectrophotometrically by measuring spectral changes of the reaction mixture with time in the visible and near-UV regions by means of a Perkin-Elmer Lambda 5 or a Cary 219 spectrophotomer. The reactions were started by mixing known volumes of prethermostated standard solutions of reagents in the thermostated (±0.05 °C) cell compartment of the spectrophotometer. Using at least a 10-fold excess of nucleophile over complex ensured first-order kinetics in any run. The reactions with dppe and dppp required the use of a HI-TECH SF3 stopped-flow spectrophotometer equipped with a Gould 054100 oscilloscope and a Radiometer REC 61

[†] Università di Messina.

[‡] University College London.

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Table I. Derived Rate Constants for the Reaction *cis*-$[PtR_2(L)_2]$ + L-L → $[PtR_2(L\text{-}L)]$ + 2L in Benzene at 303.3 K

	cis-$[Pt(CH_3)_2(Me_2SO)_2]$			*cis*-$[Pt(CH_3)_2(Me_2S)_2]$			*cis*-$[Pt(C_6H_5)_2(Me_2SO)_2]$			*cis*-$[Pt(C_6H_5)_2(Me_2S)_2]$		
L-L	$10^2k_1/s^{-1}$	k_3/k_{-1}	$k_2/M^{-1}\ s^{-1}$	$10^2k_1/s^{-1}$	k_3/k_{-1}	$k_2/M^{-1}\ s^{-1}$	$10^2k_1/s^{-1}$	k_3/k_{-1}	$k_2/M^{-1}\ s^{-1}$	$10^2k_1/s^{-1}$	k_3/k_{-1}	$k_2/M^{-1}\ s^{-1}$
bpy	0.094[a]	0.11[a]	0.0[a]	0.184[a]	0.59[a]	0.00[a]						
bpy	0.334[b]	0.14[b]	0.004[b]	0.73[b]	0.52[b]	0.00[b]						
bpy	1.12	0.17	0.006	2.34	0.60	0.00	1.40[c]	0.049[c]	0.00[c]	0.53[d]	0.68[d]	0.00[d]
bpy	3.22[e]	0.22[e]	0.114[e]	8.10[e]	0.56[e]	0.00[e]						
bpym	1.35	0.29	0.03	2.59	0.88	0.02	2.30[d]	0.092[d]	0.12[d]	0.51[d]	0.92[d]	0.00[d]
phen	1.07	0.56	0.06	2.75	1.02	0.00	2.00[c]	0.26[c]	0.00[c]	0.53[d]	1.43[d]	0.00[d]
dpte	1.16	0.66	0.16	2.88	0.99	0.05	2.50[d]	0.21[d]	0.26[d]	0.60[d]	1.65[d]	0.05[d]
dppe			226			35	2.00[c]	5.6[c]	10.0[c]	0.42[d]	0.89[d]	3.87[d]
dppp			148			28	1.90[c]	1.71[c]	9.3[c]	0.59[d]	0.77[d]	2.46[d]
$\Delta H_1^{\ddagger}$/ kcal mol^{-1} [f]		20.3 ± 0.2			21.5 ± 0.4			15.3 ± 0.4			24.1 ± 0.7	
$\Delta S_1^{\ddagger}$/ cal $K^{-1}\ mol^{-1}$ [f]		−0.7 ± 0.8			+5 ± 1			−16 ± 2			+10 ± 2	

[a] 283.2 K. [b] 293.2 K. [c] Data from ref 5. [d] Data from ref 6. [e] 313.2 K. [f] From the values of k_1 for the reaction with bpy.

potentiometric recorder. The first-order rate constants were obtained either from the slopes of the plot of $-\ln(A_\infty - A_t)$ against time t, where (A_t and A_∞) are the absorbances at time t and at the end of the reaction, respectively, or from a nonlinear least-squares fit of the experimental A_t vs t data to the expression $A_t = A_0 + (A_0 - A_\infty)\exp(-k_{obsd}t)$, with A_0 being the absorbance at time $t = 0$ and A_∞ and k_{obsd} as parameters to be optimized. The graphical methods are still employed because they provide a ready indication of any systematic departure from a simple first-order process. Activation parameters were derived from a nonlinear fit of the k/T vs T data to the Eyring equation once the individual rate constants had been separated.

Results

Whereas the preparation of *cis*-$[PtMe_2(Me_2SO)_2]$ and its isolation as white crystals are straightforward, the corresponding *cis*-$[PtMe_2(Me_2S)_2]$ could not be isolated from solution. It was therefore necessary to use instead the Me_2S-bridged dimer $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ and to convert it, in situ, to the required mononuclear complex by carrying out the reaction in the presence of an excess of Me_2S at least 50 times greater than the concentration of the complex.[8] The conversion was shown to be much more rapid than the subsequent displacement of the dimethyl sulfide by the chelating nucleophile. In $CDCl_3$ solution the ^1H NMR spectrum of the dimer changes immediately to the simpler spectrum of *cis*-$[PtMe_2(Me_2S)_2]$ (δ (Pt–CH_3) 0.644 (^2J(PtH) = 82 Hz), δ(S–CH_3) 2.39 (^3J(PtH) = 23 Hz). The presence of a separate signal for the free ligand and the absence of significant line broadening indicated that Me_2S exchange is slow with respect to the NMR time scale under these conditions.

In the presence of the bidentate ligand the electronic spectrum of the substrate changes smoothly to one that is identical with that of an authentic sample of the $[PtMe_2\ (L\text{-}L)]$ product. When L-L is one of the diimine ligands bpy, phen, or bpym, the product absorbs strongly in the visible region[9] while the starting materials are colorless, and abstract factor analysis of the spectral changes[13] indicates the presence of only one absorbing species. The products containing the thioether and the chelating phosphines do not have these highly characteristic peaks in the visible region, and the rapidity of the latter reactions does not allow a repetitive scan study with the equipment available. Nevertheless, all the spectrophotometric analyses are consistent with the simple conversion of the substrate to the product without the buildup of measurable amounts of any intermediate species.

The reactions were carried out under first-order conditions in the presence of a sufficient and known excess of the leaving group (Me_2SO or Me_2S) and the entering group (L-L), and the rate constants, k_{obsd} (Tables SI and SII) are available as supplementary material, where they are compared with k_{calcd} from the derived rate constants.

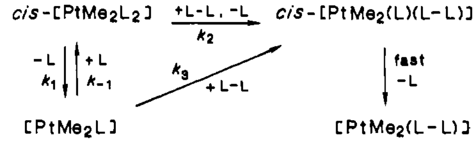
Discussion

The evidence clearly indicates that, as in the case of the analogous reactions of *cis*-$[PtPh_2(Me_2SO)_2]$ and *cis*-$[PtPh_2(Me_2S)_2]$, the rate-determining step in the displacement of the sulfur donors by the chelate is the replacement of the first ligand, the subsequent ring closing being fast. The dependence of k_{obsd} on [L] and [L-L] (L being the leaving group) is very similar to that observed in the reactions of the phenyl complexes,[5,6] the process being retarded by the free leaving group and exhibiting saturation kinetics (i.e., k_{obsd} becomes independent of [L-L] at high enough concentrations) when L-L = bpy, bpym, or phen. It can be shown that the general rate law takes the form

$$k_{obsd} = \frac{a[L\text{-}L]}{b[L] + [L\text{-}L]} + c[L\text{-}L]$$

although in the cases where L-L = dppe and dppp the process is so dominated by the contribution from the c[L-L] term that the other part of the expression could not be assessed. The best values of the constants a, b, and c, together with their standard deviations, were obtained by multiple nonlinear regression of k_{obsd} vs [L-L] and [L] according to the rate equation.

The rate law is consistent with the parallel associative and dissociative pathways



with the rate constants relating to the empirical parameters a, b, and c by the expressions $a = k_1$, $b = k_{-1}/k_3$, and $c = k_2$. Values of these rate constants are collected in Table I, where they are compared with the previously published values for the corresponding phenyl complexes.

The general pattern of behavior is much the same in both sets of substrates; i.e., there is a major dissociatively activated pathway that may be accompanied by, or occasionally even swamped by, a parallel associatively activated pathway depending upon the nucleophilicity of the entering group. The biggest and most obvious difference between the diphenyl and dimethyl complexes is the greater importance of the associatively activated pathway in the latter case. With the entering phosphines, the k_2 pathway dominates completely, and in the case of the Me_2SO-containing substrate, where the effect is much more pronounced, a value can be obtained for k_2 for all nucleophiles, even the nitrogen donors, and the nucleophilic discrimination is quite significant. The displacement of Me_2S is less susceptible to associative activation, and the relative importance of the associative pathway is only doubled on going from Ph to Me. The increasing associative lability is probably of steric origin, the smaller methyl groups causing less congestion in the transition state. The mutual labilization of a pair of cis sulfoxides, which is observed when

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substitution is associative[14,15] but not when it is dissociative,[5] is consequently seen. The smaller methyl groups permit the necessary compact transition state. The changes in the reactivity toward dissociative substitution are less marked. At 30 °C, the dissociative lability of *cis*-$[PtMe_2(Me_2S)_2]$ is about twice that of the Me_2SO analogue. This is the opposite of what is observed in the diphenyl analogues, but there the enthalpies of activation differ so much from one to another that the relative reactivities will depend upon the temperature of the reaction. The marked difference between the activation parameters for the dissociation of Me_2SO and Me_2S from their diphenyl complexes is not observed for the dimethyl analogues, and while the displacement of Me_2S does have a larger value for ΔS^*, the difference is too small to be significant. The nucleophilic discrimination of the $[PtMe_2(Me_2SO)]$ intermediate is somewhat greater than that observed for $[PtMe_2(Me_2S)]$, but in the absence of data for phosphine nucleophiles (masked by the preponderant associative pathway), the range of nucleophilicity studied is too narrow for significant comment to be made.

It must be concluded, therefore, that the change from C_6H_5 to CH_3 does not greatly affect the ease with which the dissociative activation takes place and that the stabilization of the three-coordinate intermediate by interaction between Pt and the ortho hydrogens in the phenyl ring plays little, if any, part in promoting the dissociative nature of the process.

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Registry No. Bpy, 366-18-7; phen, 66-71-7; dppp, 6737-42-4; bpym, 34671-83-5; dppe, 1663-45-2; dpte, 622-20-8; *cis*-$[PtMe_2(Me_2SO)_2]$, 70423-98-2; *cis*-$[PtMe_2(Me_2S)_2]$, 87145-38-8.

Supplementary Material Available: Tables SI and SII, giving primary kinetic data (k_{obsd}/s^{-1} and k_{calcd}/s^{-1}) (10 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
Colorado State University, Fort Collins, Colorado 80523

Preparation and Characterization of Palladium(II) and Platinum(II) $OTeF_5$ Complexes

Mark R. Colsman, Mark C. Manning, Oren P. Anderson,
and Steven H. Strauss*[1]

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Table I. Details of the X-ray Diffraction Study for $Pt(OTeF_5)_2(NBD)$

mol formula	$C_7H_8F_{10}O_2PtTe_2$
mol wt	764.42
space group	$P2_1/c$
unit cell	
a, Å	9.197 (2)
b, Å	14.842 (4)
c, Å	10.486 (3)
β, deg	93.78 (2)
unit cell vol, $Å^3$	1428.2 (5)
Z	4
calcd density, g cm^{-3}	3.56
cryst dimens, mm	0.08 × 0.30 × 0.125
data collcn temp, °C	−130
radiation (λ, Å)	Mo Kα (0.71073)
monochromator	graphite
abs coeff, cm^{-1}	145.8
2θ range, deg	3.5–50
reflcns	$\pm h,k \geq 0,l \geq 0$
no. of reflcns with $I > 2\sigma(I)$	2171
total no. of reflcns measd	2793
scan type	θ–2θ
scan speed, deg min^{-1}	variable (2–30)
data/param ratio	10.9
R	0.0318
R_w	0.0460
GOF	2.475
g	2.1×10^{-4} (refined)
slope of normal probability plot	1.970

Pentafluoroorthotellurate ($OTeF_5^-$), or teflate, first prepared in 1964 in the form of its conjugate acid $HOTeF_5$,[2] has been well characterized as a bulky pseudohalide.[3-5] Although it has an ionic radius larger than iodide,[6] the $OTeF_5$ radical possesses an electronegativity equal to that of fluorine.[7] However, while $OTeF_5$ has proven to be a versatile, bulky, fluorine-like substitute for binary main-group and high-valent transition-metal fluorides,[3-5] the $OTeF_5^-$ anion does not display fluoride-like properties. For example, the hydrogen bond strength in the $H(OTeF_5)_2^-$ anion is much weaker than that in bifluoride, HF_2^-.[8] Nevertheless, the electronic and structural properties of $OTeF_5^-$ are sufficiently different from those of other anions[9] that its potential as an unusual ligand for low-valent transition metals in organometallic complexes warrants exploration. Our first reports in this area detailed the preparation, characterization, and reactivity of metal carbonyl teflates such as $Mn(CO)_5(OTeF_5)$.[10] In this paper we report the synthesis and spectral characterization of $Pt(OTeF_5)_2(NBD)$ (NBD = norbornadiene) and $Pd(OTeF_5)_2(C_6H_5CN)_2$ and describe the molecular structure of the platinum complex.

Experimental Section

The general air-free procedures for the handling of these reactive, hygroscopic compounds and for obtaining IR and NMR spectral data have been described elsewhere.[8,10,11] The compound $[AgOTeF_5(tol)_2]_2$ (tol = toluene) was prepared by published procedures.[12]

$Pt(OTeF_5)_2(NBD)$. Solid $PtCl_2(NBD)$[13] (0.479 g, 1.34 mmol) was stirred for 12 h at 22 °C with a dichloromethane solution (20 mL) of $[AgOTeF_5(tol)_2]_2$ (1.42 g, 1.34 mmol). The AgCl precipitate was removed by filtration and washed with dichloromethane. The washings were combined with the filtrate, and the solvent was removed under vacuum at 22 °C. The white solid was recrystallized from a minimum of dichloromethane (75% yield). ^1H NMR (CD_2Cl_2, 22 °C, Me_4Si internal standard): δ 1.64 (2 H, methylene), 4.55 (2 H, bridgehead), 5.58 (4 H, olefin); $J_{PtH(olefin)} = 69.8$ Hz. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 22 °C, Me_4Si internal standard): δ 49.5 (methylene), 68.6 (bridgehead), 76.1 (olefin); $J_{PtC(olefin)} = 136$ Hz. ^{19}F NMR (CH_2Cl_2, 22 °C, $CFCl_3$ external standard): AB_4X pattern (X = ^{125}Te, 7.0% natural abundance, I = $^1/_2$); δ_A −33.2, δ_B −39.7; $J_{AB} = 166$ Hz, $J_{BX} = 3662$ Hz. $^{125}Te\{^1H\}$ NMR (CH_2Cl_2, 22 °C, aqueous $Te(OH)_6$ external standard): XAB_4 pattern (A, B = ^{19}F); δ −107; $J_{XA} = 3185$ Hz, $J_{XB} = 3657$ Hz. $^{195}Pt\{^1H\}$ NMR (CH_2Cl_2, 22 °C, aqueous K_2PtCl_4 external standard): δ −2834 (broad singlet, $\Delta\nu_{1/2} = 66$ Hz).

$Pd(OTeF_5)_2(C_6H_5CN)_2$. This compound was prepared as above by using $PdCl_2(C_6H_5CN)_2$[14] in place of $PtCl_2(NBD)$. It crystallized from

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