(metal:ligand) species, and no improvement occurred when other species were included. All equilibria were established quickly.

A listing of the respective log *K* values together with the previously determined values for nickel and copper are given in Table VIII, and a representative set of potentiometric curves (for the complexes of **3**) are reproduced in Figure 4. In general, the log *K* values follow the expected Irving–Williams[30] order of $Co(II) < Ni(II) < Cu(II) > Zn(II)$.

As mentioned previously, with nickel(II) the stability reaches a peak for the 16-membered ring complex. From consideration of the X-ray structures of the nickel complexes of **2** and **3** together with the literature values for typical nickel–ether oxygen and nickel–nitrogen bond distances, it seems likely that the 16-membered macrocycle provides the ring of least strain for the nickel ion.[3,5] For copper and zinc, the absence of a definite peak in the respective log *K* values can be rationalized in terms of the proposed solution structures of these complexes. For copper, the metal ion is very likely not completely encircled by the donor atoms of the respective macrocycles, and, indeed, different coordination geometries may well occur along the series of complexes.[6] For zinc, the evidence discussed above suggests that the ether oxygen donors of each macrocycle do not coordinate. Thus for both these metal-ion systems no clear ring-size discrimination effects would be expected and none are observed.

Acknowledgment. L.F.L. expresses thanks to Professor G. Anderegg (ETH, Zürich) and Dr. J. T. Baker (Roche Research Institute of Marine Pharmacology, Sydney) for assistance. Acknowledgment is made to the Australian Research Grants Committee for support and the Australian Institute of Nuclear Science and Engineering for a travel grant. M.M. and P.A.T. thank the Science Research Council (U.K.) for diffractometer equipment and computing facilities.

Registry No. **1**, 65639-47-6; **2**, 65639-43-2; **3**, 65639-49-8; **4**, 66793-29-1; **7**, 66793-30-4; $Co(L_2)(SCN)_2$, 74381-17-2; $Co(L_2)Br_2$, 74381-18-3; $Co(L_3)(SCN)_2$, 74381-19-4; $Co(L_4)(SCN)_2$, 74381-20-7; $Co(L_4)Br_2$, 74381-21-8; $Co(L_4)Cl_2$, 74381-22-9; $Zn(L_1)I_2$, 74381-23-0; $Cd(L_1)I_2$, 74381-24-1; $Zn(L_2)I_2$, 74381-25-2; $Cd(L_2)I_2$, 74381-26-3; $Zn(L_3)I_2$, 74381-27-4; $Cd(L_3)I_2$, 74381-28-5; $Zn(L_4)I_2$, 74381-29-6; $Cd(L_4)I_2$, 74381-30-9; $Zn(L_7)I_2$, 74381-31-0; $Zn(L_2)Cl_2$, 74381-32-1; $Zn(L_4)Cl_2$, 74381-33-2; $Zn(L_5)I_2$, 74397-15-2; $Zn(L_6)I_2$, 74397-16-3; $Zn(L_7)Cl_2$, 74381-34-3; $Cd(L_5)I_2$, 74381-35-4; $Cd(L_6)I_2$, 74397-17-4.

Supplementary Material Available: Listings of analytical data for the complexes and structure factor tables for the X-ray structure determination of $ZnLI_2$ ($L = 7$) (10 pages). Ordering information is given on any current masthead page.

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[30] Irving, H.; Williams, R. J. P. *J. Chem. Soc.* **1953**, 3192.

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Kinetics and Mechanism of the Reaction of Palladium(II) Complexes of *o*-(Diphenylphosphino)thioanisole and *o*-(Diphenylphosphino)selenoanisole with Nucleophiles Thiocyanate and Iodide. Carbon-13 NMR Spectroscopy of the Methyl–Heteroatom Complexes and X-ray Structural Characterization of Diiodobis[*o*-(diphenylphosphino)benzenethiolato]dipalladium(II)[1]

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and UTTARAYAN BAGCHI

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The kinetics of the reaction of the nucleophiles thiocyanate and iodide with complexes PdX_2(*o*-$MeSC_6H_4PPh_2$) (X = SCN, I) show a rate law rate = $k_2[PdX_2(o\text{-}MeSC_6H_4PPh_2)][X^-]$. Second-order rate constants k_2 for the thiocyanate reaction have been measured, and the activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are 22.9 ± 1.0 kcal/mol and −9.2 ± 2.1 cal/mol. For the selenium analogue complex these respective values are 18.9 ± 1.3 kcal/mol and −12.9 ± 2.3 cal/mol. With iodide as nucleophile an equilibrium condition is established. Rates are calculated from the data both for the demethylation and for the reverse addition of methyl iodide. The alkylation reaction is approximately 50 times faster. The product from the iodide demethylation reaction is considered to be the anion $[PdI_2(o\text{-}SC_6H_4PPh_2)]^-$ on the basis of visible spectroscopy. The mechanism of the nucleophile-induced demethylation reaction resembles the Zeisel ether cleavage.

^1H and ^{13}C NMR parameters have been measured and compared both for the free ligands *o*-$MeSC_6H_4PPh_2$, *o*-$MeSeC_6H_4PPh_2$, *o*-$MeOC_6H_4PPh_2$, and *o*-$Me_2NC_6H_4PPh_2$ and for a series of transition-metal complexes of these ligands. Complexation causes a small downfield shift in the position of the ^1H NMR resonance of the methyl group and a larger downfield shift in the ^{13}C NMR parameter. These data show that complexation of the heteroatom causes an increased carbonium ion character at the methyl carbon.

New complexes $RuCl_2$(*o*-$MeSC_6H_4PPh_2$)$_2$ and $RuCl_2$(*o*-$MeSeC_6H_4PPh_2$)$_2$ have been prepared with the S and Se atoms complexed to Ru(II). The mixed ligand *o*-$MeSeC_6H_4SMe$ forms a chelate complex $PdCl_2$(*o*-$MeSeC_6H_4SMe$). ^1H, ^{13}C, and ^{77}Se NMR spectra of this ligand are measured and compared with the ^1H and ^{13}C NMR spectra of the palladium complex.

The compound $[PdI(o\text{-}SC_6H_4PPh_2)]_2$, obtained from thermolysis of PdI_2(*o*-$MeSC_6H_4PPh_2$), crystallizes with 4 molecules per unit cell in a $P\bar{1}$ space group. Cell parameters are $a = 19.870$ (6) Å, $b = 14.754$ (5) Å, $c = 14.856$ (6) Å, $\cos\alpha = -0.2643$ (6), $\cos\beta = -0.2226$ (4), and $\cos\gamma = 0.0089$ (4). Refinement of the structure to $R = 0.056$ shows two dimeric molecules with Pd–Pd separations of 2.964 and 2.916 Å and S–S separations of 2.972 and 3.006 Å. The molecules are bridged by double thiolato bridges, and the folding along the S–S line leads to dihedral angles of 74.3 and 79.8°. The Pd_2S_2 rhombus is unsymmetrical with the Pd–S bonds trans to the phosphorus atom being slightly longer than those trans

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[1] A preliminary communication of this work has been published: Roundhill, D. M.; Beaulieu, W. B.; Bagchi, U. *J. Am. Chem. Soc.* **1979**, *101*, 5428.

to the iodine. The structure is compared with previous thiolato-bridged d^8 metal dimers and higher aggregates.

Results and Discussion

Demethylation of Methyl Thioether Complexes. This project was begun to answer two specific questions. The first goal is to deduce the mechanism of the demethylation of transition-metal methyl thioether complexes. The second aim is to compare the energetics of this reaction with the biologically important methylation function of *S*-adenosylmethionine.

The conversion of methyl thioether complexes into thiolato compounds by the loss of a methyl group has been reported for a large range of compounds.[2] The reaction with nonfluorinated ligands is commonly found to occur under high-temperature conditions and in only a few cases has an attempt been made to determine the fate of the alkyl group. The reaction has frequently been effected by thermolysis in DMF, and the product has been identified as the thiolato-bridged dimer. Mechanistically there has been a suggestion that an ionic pathway is involved, with the reaction resembling the Zeisel ether cleavage.[2f] In a similar chemistry Shaw has found that the ether complex $PtCl_2(o\text{-}MeOC_6H_4PPh_2)$ will undergo dealkylation to give $PtCl_2(o\text{-}OC_6H_4PPh_2)$.[3] In a comment about the reaction pathway Shaw observed that the addition of halide had minimal effect on the dealkylation. There has hitherto been no kinetic investigation of these transition-metal-induced demethylations, and in view of current parallel interest in methylsulfonium and similar complexes[4] we decided to investigate more fully one of these demethylation reactions.

Methyl transfer from donor to acceptor is an important biological process. The most frequent donor in these systems is *S*-adenosylmethionine. The biochemistry of the methyl transfer from this compound has been of major interest.[5] The chemistry parallels that of methylsulfonium compounds where the methyl group is removed as a carbonium ion by an incoming nucleophile.[6] Our data has been obtained by using a methyl group on a neutral coordinated methyl thioether as electrophile, and the results allow us to compare the metal-induced demethylation reaction with that from a sulfonium ion center.

Table I. Rate Data for the Reaction of $(o\text{-}Ph_2PC_6H_4SMe)Pd(SCN)_2$ with SCN^- in CD_3CN Solvent[a]

T, °C	$[NaSCN]_0$, M	10^4k_1(obsd), s^{-1}
75	0.213	3.25
75	0.420	4.15
75	0.635	5.79
65	0.222	1.21
55	0.222	0.38

[a] $[(o\text{-}Ph_2PC_6H_4SMe)Pd(SCN)_2] = 0.020$ M.

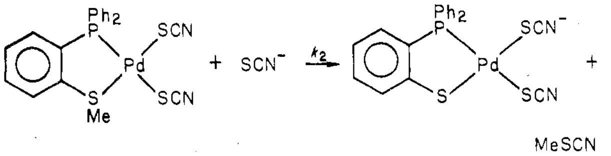
Table II. Rate Data for the Demethylation of $(o\text{-}Ph_2PC_6H_4SeMe)Pd(SCN)_2$ with SCN^- in CD_3CN/CH_2Cl_2 (3:1) Solvent[a]

T, °C	$[NaSCN]_0$, M	10^3k_1(obsd), s^{-1}
55	0.225	2.51
45	0.225	1.05
35	0.231	0.353

[a] $[(o\text{-}Ph_2PC_6H_4SeMe)Pd(SCN)_2] = 0.023$ M.

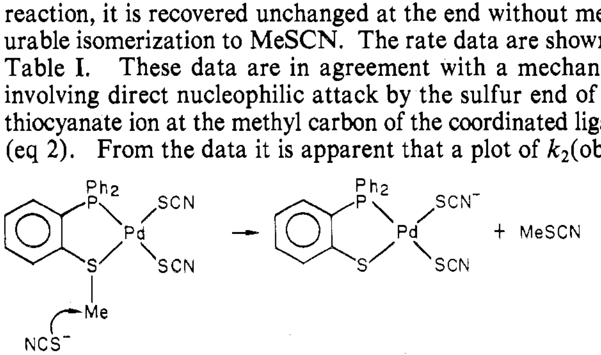
Kinetic Studies. We have found that in addition to the previous reports of refluxing DMF conditions, the demethylation can be carried out at temperatures down to 55 °C in the presence of a nucleophile such as thiocyanate or iodide. The rates have been studied for the reactions of $Pd(SCN)_2(o\text{-}MeSC_6H_4PPh_2)$ with SCN^- and $PdI_2(o\text{-}MeSC_6H_4PPh_2)$ with I^-. As control experiments we have confirmed that the free ligand $o\text{-}MeSC_6H_4PPh_2$ demethylates insignificantly under the conditions used for demethylation with the palladium complex. In a related series of experiments we find that the complex $Pd(SCN)_2(o\text{-}MeSC_6H_4PPh_2)$ demethylates within 20 min in refluxing Me_2SO and within 2 h under reflux with DMF and benzonitrile. The complex does not, however, demethylate significantly after 90 min in refluxing acetonitrile, and there is no demethylation with the electrophile mercuric chloride or under UV irradiation.

The reaction between $Pd(SCN)_2(o\text{-}MeSC_6H_4PPh_2)$ and SCN^- follows the rate law rate = k_2[complex]$[SCN^-]$ (eq 1).



(1)

The formation of MeSCN has been verified by comparison of its ^1H NMR chemical shift (δ 2.46) and its gas chromatographic retention time against those of authentic samples. The isomer MeSCN is the one formed directly in the reaction. There is no observable trace of the isomer MeNCS in the product, and if MeNCS is added at the beginning of the reaction, it is recovered unchanged at the end without measurable isomerization to MeSCN. The rate data are shown in Table I. These data are in agreement with a mechanism involving direct nucleophilic attack by the sulfur end of the thiocyanate ion at the methyl carbon of the coordinated ligand (eq 2). From the data it is apparent that a plot of k_2(obsd) against [NaSCN] is not linear. We believe this deviation is a consequence of a noncorrespondence between $[SCN^-]$ and [NaSCN]. This difference for ionic reactions in nonaqueous solvents has been frequently observed before and arises because effects such as ion pairing cause the activity of the thiocyanate ion to be less than that obtained simply by using the value for [NaSCN].[7] The degree of dissociation has previously been



(2)

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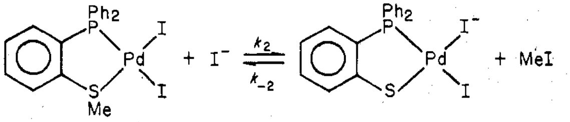
related to both the dielectric constant and donor number of the particular solvent and is roughly proportional to both these quantities. From these data it is apparent that there will be considerable ion pairing of NaSCN in this solvent. For the solvent Me_2SO, however, dissociation should be more complete, and this is borne out by the ^{23}Na chemical-shift data for NaSCN in this solvent.[8] This should lead to closer linearity between k(obsd) and [SCN^-]. At 77.6 ± 0.2 °C the respective rate constants K_2(obsd) in $Me_2SO\text{-}d_6/CH_2Cl_2$ (3:1) solvent are 2.26×10^{-4} and 4.06×10^{-4} s^{-1} for NaSCN concentrations of 0.222 and 0.387 M. With the approximation that [SCN^-] = [NaSCN], the rate constants k_2 are 1.02×10^{-3} and 1.05×10^{-3} M^{-1} s^{-1}, showing the ion pairing effect to be negligible in this solvent. From an Eyring plot of the data in Table I the values of ΔH^* and ΔS^* are 22.9 ± 1.0 kcal/mol and −9.2 ± 2.1 cal/mol, respectively.

We have also measured the rate of reaction of the selenium analogue $Pd(SCN)_2(o\text{-}MeSeC_6H_4PPh_2)$ with SCN^- (Table II). These data confirm the previous suggestion that the rate is faster,[1g] the enhancement being 66-fold at 55 °C. The respective activation parameters ΔH^* and ΔS^* are 18.9 ± 1.3 kcal/mol and −12.9 ± 2.3 cal/mol, considerably smaller than the corresponding values for the thioether complex.

For the reaction with the nucleophile iodide (eq 3) the

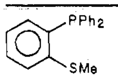
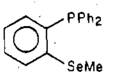
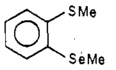
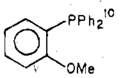
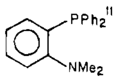


(3)

chemistry is more complicated. The product, methyl iodide, is a stronger alkylating agent than methyl thiocyanate and thus the reaction does not go to completion because the competing back-reaction leads to the establishment of an equilibrium condition. The complex $PdI_2(o\text{-}MeSC_6H_4PPh_2)$ is less soluble in CD_3CN than is the thiocyanate analogue, and hence the kinetic data have been obtained in a $CDCl_3/CD_3CN$ (1:2.5) mixed solvent. With the initial rate method described in the Experimental Section, the respective values k_2 and k_{-2} are found to be 3.4×10^{-3} and 2.5×10^{-1} M^{-1} s^{-1}, and hence $K = 1.4 \times 10^{-2}$ s^{-1} (77 °C). This equilibrium constant can be measured independently by using the NMR method to measure the amounts of $PdI_2(o\text{-}MeSC_6H_4PPh_2)$ and MeI present after equilibrium has been attained. After establishment of equilibrium (75-min reaction time in a closed NMR tube) with three solutions containing $PdI_2(o\text{-}MeSC_6H_4PPh_2)$ (0.01 M) and NaI (0.10 M, 0.30 M, and 0.42 M, respectively), the final concentrations of the methylated complex are 6.7, 5.8, and 4.8×10^{-3} M. This leads to a value for K of $(1.8 \pm 0.35) \times 10^{-2}$. This alkylation reaction has been investigated by earlier workers, and the kinetics of one such reaction has recently been reported.[9]

Our data are thus in agreement with the previous suggestion that demethylation from methyl thioether– and methyl selenoether–palladium(II) complexes occurs in a manner similar to the Zeisel ether cleavage. Quantitative comparison with the energetics of demethylation from S-adenosylmethionine is somewhat imprecise because of differences in reaction conditions for the two studies, but this value of 23.6 kcal/mol for E_a compares very favorably with the value of 23.8 kcal/mol found for S-adenosylmethionine analogue compounds. Both reactions involve nucleophilic attack at a saturated carbon, and the close similarity of the activation parameters shows that coordination of thioether in an uncharged palladium(II) complex can create a methyl group of comparable electrophilicity with one on a sulfonium ion.

Table III. ^1H and ^{13}NMR CHemical Shift Data for the Me Groups

	δ(Me_4Si)	
	^{13}C	^1H
	17.3 (d) ($^4J(^{13}C\text{-}^{31}P)$ = 7 Hz)	2.39
$Pd(SCN)_2(o\text{-}MeSC_6H_4PPh_2)$	29.8 (s)	2.81
$PdI_2(o\text{-}MeSC_6H_4PPh_2)$	31.1 (s)	2.96
$Pt(SMe)_2(PPh_3)_2$	17.4 (s), 13.3 (s)	
$RuCl_2(o\text{-}MeSC_6H_4PPh_2)_2$	25.3 (s)	1.90
	8.3 (d) ($^4J(^{13}C\text{-}^{31}P)$ = 11 Hz)	2.23 ($^2J(^1H\text{-}^{77}Se)$ = 12 Hz)
$Pd(SCN)_2(o\text{-}MeSeC_6H_4PPh_2)$	22.7	2.69
	7.3 ($^1J(^{13}C\text{-}^{77}Se)$ = 64 Hz), 15.8 (s)	2.38 (s)-(SMe), 2.22 (s) (SeMe) ($^2J(^1H\text{-}^{77}Se)$ = 13 Hz)
$PdCl_2(o\text{-}MeSeC_6H_4SMe)$	22.7 (s) (SeMe), 29.4 (s) (SMe)	2.61 (s) (SMe), 2.53 (s) (SeMe)
	55.4 (s)	3.80
$RuCl_2(o\text{-}MeOC_6H_4PPh_2)_2$[10]	61.4 (s)	4.63
	45.7 (s)	2.65
$PdCl_2(o\text{-}Me_2NC_6H_4PPh_2)$	55.6 (s)	
$[RhCl_2(o\text{-}Me_2NC_6H_4\text{-}PPh_2)_2]SbF_6$[11]	54.1 (s)	3.22
$[Pt(o\text{-}Me_2NC_6H_4PPh_2)_2]\text{-}(ClO_4)_2$[10]	54.9 (s)	3.36

^1H and ^{13}C NMR Data. From our kinetic measurements we conclude that coordination of the methylthio group to palladium(II) causes the carbon of the methyl group to acquire increased carbonium ion character. This transfer of electron density from ligand to metal is in concurrence with ^1H NMR studies of the methyl protons where they show a downfield shift on coordination, suggestive of increased acidity at that atom. These data are collected in Table III. These shifts are quite small, and in one case, $RuCl_2(o\text{-}MeSC_6H_4PPh_2)_2$, there is a shift in the opposite direction. It is of interest to note the correlation that this compound does not demethylate under the experimental conditions successfully used to demethylate $Pd(SCN)_2(o\text{-}MeSC_6H_4PPh_2)$.

The ^{13}C nucleus of the methyl group should show a more marked chemical shift difference on coordination of the sulfur or selenium atom, and the shift should be better correlated to carbonium ion character than the ^1H NMR shift. As expected, the methyl ^{13}C NMR shifts of these ligands upon coordination to a metal show larger shifts than the ^1H resonance. In each case the shift is to lower field which is to be expected if coordination increases carbonium ion character. The shift is in the 10–15-ppm range, and for the limited number of examples shown in Table III there is little variation in magnitude.

The chemical shifts of the uncoordinated ligands having a SMe group fall in the range (δ 15–18) which is in agreement with literature data. For the complex $Pt(SMe)_2(PPh_3)_2$ the

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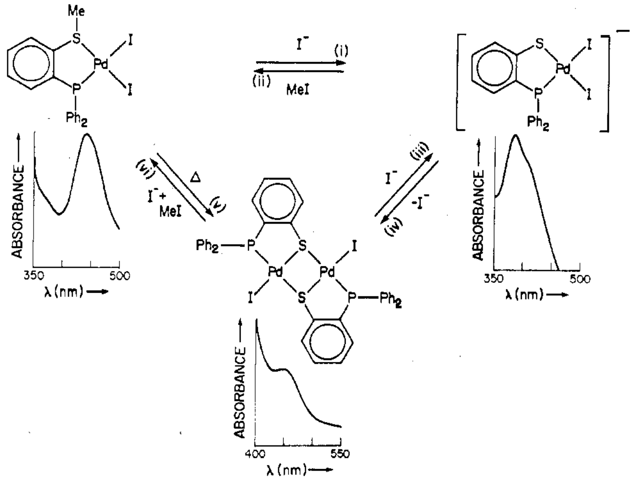

Figure 1. Interconversion reactions and electronic spectra of reactants and products.

cis and trans isomers show resonances at δ 17.4 and 13.3, which is close to the range found for the ligands. This position is apparently consistent for a binary substituted SMe group, irrespective of whether the SMe is bonded to a carbon or a platinum, and the shift to δ 29–31 in the complexes is due to the ternary coordination of the sulfur and is not just simply due to metal coordination.

A comment is required on the observation that the ^{13}C chemical shift of the methyl group in $RuCl_2(o\text{-}MeSC_6H_4PPh_2)_2$ is found at δ 25.3. This represents a shift of 8 ppm from the compound $o\text{-}MeSC_6H_4PPh_2$ which is less than that found for $PdX_2(o\text{-}MeSC_6H_4PPh_2)$ (X = SCN, I). This smaller difference implies decreased carbonium ion character; nevertheless it is significant that a *downfield* shift is observed. This direction is the opposite from that found for the ^1H NMR shift of the methyl group. It is apparent from the ^{13}C NMR spectrum that coordination of the thioether to ruthenium(II) causes the methyl group to become electron poor and not the opposite in a d_π back-bonding type of interaction. We believe that the upfield shift for the methyl resonance in the ^1H NMR spectrum is anomalous and does not represent a *through bond* type of shielding of the nucleus. A more likely explanation is an upfield shielding caused by a through space interaction between the methyl hydrogens and an adjacent phenyl ring, a situation more likely in an octahedral complex of bis[*o*-(diphenylphosphino)thioanisole].

In Table III we also correlate $\delta(^1H)$ and $\delta(^{13}C)$ NMR shifts for other heteroatom complexes (O and N).[10,11] Similar results are found. In each case there is a downfield shift for both the ^1H and ^{13}C resonances in the CH_3 group upon coordination of the heteroatom to the metal center. The change in ^{13}C shift position on coordination falls in the 6–10-ppm range. This is smaller than that observed for the thioether complexes. For the dimethylamino complexes this may be a consequence of the electron density being spread over two methyl groups, but for the ether complex $RuCl_2(o\text{-}MeOC_6H_4PPh_2)_2$ the carbonium ion character caused by coordination of the OMe group to Ru(II) is significantly lower.

Palladium Thiolate Complexes. In Figure 1 we show interconversion reactions occurring in the demethylation reaction of $PdI_2(o\text{-}MeSC_6H_4PPh_2)$. We propose that the final product in these iodide reactions is the complex anion $[PdI_2(o\text{-}SC_6H_4PPh_2)]^-$. This species is being claimed on the basis of spectroscopic evidence and differs from the dimer product $[PdI(o\text{-}SC_6H_4PPh_2)]_2$ obtained by heating $PdI_2(o\text{-}MeSC_6H_4PPh_2)$ in DMF solvent. Under our demethylation conditions an excess of iodide is present in the reaction mixture, and this causes an iodide ion to coordinate to palladium in preference to a bridging thiolate group. A solution of this anion has been prepared by reacting $PdI_2(o\text{-}MeSC_6H_4PPh_2)$ with excess I^- in an open system where the methyl iodide escapes, and the electronic spectrum (Figure 1) shows a band at 390 nm with a shoulder at 410 nm. This spectrum differs from those of both $PdI_2(o\text{-}MeSC_6H_4PPh_2)$ and $[PdI(o\text{-}SC_6H_4PPh_2)]_2$ which show absorptions at 450 and 460 nm, respectively. If we assign these electronic bands to $M \leftarrow I$ (LMCT) transitions, the higher energy band is to be expected in the anion, where electrons are being transferred from the iodine to a negatively charged metal center.

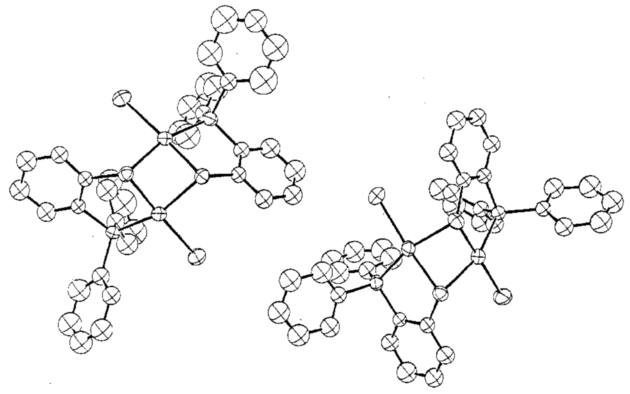

Figure 2. ORTEP drawing of the two molecules of $[PdI(o\text{-}SC_6H_4PPh_2)]_2$.

As shown in Figure 1, these three complexes are interconvertible. We have separately observed five of the six reactions and spectral changes. Step iv has not been achieved quantitatively because even small amounts of iodide present in the reaction mixture cause dimer cleavage. Interestingly the pure dimer does not readily react with methyl iodide. Addition of iodide, however, causes the methylation to be facile. This difference is due to initial dimer cleavage by iodide, leading to a binary nonbridging thiolate ligand in an anionic complex. Such a compound has a nucleophilic electron pair on sulfur available for electrophilic attack. This proposed pathway and discussion are based on the concept that the complex $[PdI(o\text{-}SC_6H_4PPh_2)]_2$ is bridged through the thiolate and not the iodide. In order to verify this fact we have prepared the complex by the thermal demethylation of $PdI_2(o\text{-}MeSC_6H_4PPh_2)$ in DMF solvent and have characterized the product by single-crystal X-ray methods.

Structure of $[PdI(o\text{-}SC_6H_4PPh_2)]_2$. The compound $[PdI(o\text{-}SC_6H_4PPh_2)]_2$ crystallizes with 4 molecules per unit cell. The crystal symmetry is $P\bar{1}$, and the structure has been solved for the two nonequivalent molecules. The palladiums are bridged by thiolates, and the iodide atoms take up the nonbridging positions at the end of each dimer unit. An ORTEP view of the dimers is shown in Figure 2. In Table IV we show the positional and thermal parameters for the nonhydrogen atoms for the molecules, and in Table V we compare the bond distances and angles in the two separate $[PdI(o\text{-}SC_6H_4PPh_2)]_2$ molecules. Included in the list are the nonbonded Pd···Pd and S···S separations, as well as the dihedral angles between the palladium coordination planes. The coordination about each palladium is planar. The molecules are folded along the S–S axis leading to a dihedral angle between these coordination planes of 77 (3)°.[12]

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[10] Rauchfuss, T. B.; Patino, F. T.; Roundhill, D. M. *Inorg. Chem.* **1975**, *14*, 652.

[11] Rauchfuss, T. B.; Roundhill, D. M. *J. Am. Chem. Soc.* **1974**, *96*, 3098.

[12] From Table V it is apparent that there are significant differences in the bond distances and angles in the two molecules. The numbers used in this discussion are an average of the two, and the errors used represent the observed spread and not the accuracy involved in each separate determination.

Table IV. Positional and Thermal Parameters for All Nonhydrogen Atoms in $[PdI(o\text{-}SC_6H_4PPh_2)]_2$

atom	*x*	*y*	*z*	*B*(1,1)	*B*(2,2)	*B*(3,3)	*B*(1,2)	*B*(1,3)	*B*(2,3)
Pd1	0.10808 (6)	0.96060 (8)	0.62525 (9)	0.00197 (5)	0.00390 (8)	0.00458 (9)	0.00003 (4)	0.00097 (5)	0.00162 (6)
Pd2	0.01153 (6)	0.83304 (8)	0.66632 (9)	0.00193 (4)	0.00373 (8)	0.00459 (9)	−0.00003 (4)	0.00087 (5)	0.00148 (6)
I1	0.24211 (6)	0.96677 (8)	0.6690 (1)	0.00193 (4)	0.00581 (9)	0.0119 (1)	0.00001 (4)	0.00130 (5)	0.00277 (8)
I2	−0.07670 (6)	0.88374 (8)	0.77355 (9)	0.00335 (5)	0.00657 (9)	0.0080 (1)	0.00065 (5)	0.00309 (5)	0.00254 (7)
S1	−0.0099 (2)	0.9504 (3)	0.5823 (3)	0.0017 (1)	0.0042 (3)	0.0036 (3)	0.0003 (1)	0.0004 (2)	0.0012 (2)
S2	0.0054 (2)	0.7936 (3)	0.5638 (3)	0.0021 (1)	0.0035 (2)	0.0039 (3)	0.0002 (1)	0.0010 (2)	0.0009 (2)
P1	0.1018 (2)	1.1112 (3)	0.7005 (3)	0.0020 (1)	0.0031 (2)	0.0054 (3)	−0.0002 (1)	0.0009 (2)	0.0012 (2)
P2	0.0600 (2)	0.7228 (3)	0.7344 (3)	0.0021 (1)	0.0035 (3)	0.0047 (3)	−0.0000 (2)	0.0006 (2)	0.0016 (2)
Pd3	0.61098 (6)	0.34603 (8)	0.62517 (9)	0.00210 (5)	0.00359 (8)	0.0050 (1)	0.00036 (4)	0.00105 (5)	0.00117 (6)
Pd4	0.51098 (6)	0.49104 (8)	0.65709 (9)	0.00186 (4)	0.00360 (8)	0.0052 (1)	0.00035 (4)	0.00065 (5)	0.00109 (6)
I3	0.74406 (6)	0.36901 (8)	0.6876 (1)	0.00200 (4)	0.00640 (9)	0.0112 (1)	0.00049 (4)	0.00135 (5)	0.00392 (8)
I4	0.42199 (6)	0.49186 (8)	0.75555 (9)	0.00275 (5)	0.00614 (9)	0.0085 (1)	0.00079 (4)	0.00248 (5)	0.00204 (7)
S3	0.4938 (2)	0.3272 (3)	0.5604 (3)	0.0023 (1)	0.0038 (3)	0.0042 (3)	0.0001 (1)	0.0001 (2)	0.0010 (2)
S4	0.5915 (2)	0.4787 (3)	0.5579 (3)	0.0025 (2)	0.0037 (2)	0.0042 (3)	0.0002 (1)	0.0009 (2)	0.0014 (2)
P3	0.6006 (2)	0.2400 (3)	0.7047 (3)	0.0018 (1)	0.0033 (2)	0.0044 (3)	0.0002 (1)	0.0007 (2)	0.0011 (2)
P4	0.5578 (2)	0.6358 (3)	0.7289 (3)	0.0020 (1)	0.0033 (3)	0.0043 (3)	0.0002 (1)	0.0005 (2)	0.0005 (2)

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
C1	0.0090 (8)	1.134 (1)	0.683 (1)	3.0 (3)	C37	0.5085 (8)	0.208 (1)	0.682 (1)	3.2 (3)
C2	−0.0375 (7)	1.060 (1)	0.641 (1)	2.8 (3)	C38	0.4627 (8)	0.253 (1)	0.626 (1)	3.0 (3)
C3	−0.1088 (8)	1.070 (1)	0.634 (1)	3.7 (4)	C39	0.3923 (9)	0.239 (1)	0.611 (1)	4.5 (4)
C4	−0.1610 (9)	1.161 (1)	0.672 (1)	4.9 (4)	C40	0.3665 (9)	0.177 (1)	0.653 (1)	4.7 (4)
C5	−0.083 (1)	1.239 (1)	0.717 (1)	5.1 (4)	C41	0.4122 (9)	0.131 (1)	0.710 (1)	4.5 (4)
C6	−0.0120 (9)	1.222 (1)	0.721 (1)	4.5 (4)	C42	0.4833 (8)	0.144 (1)	0.723 (1)	3.9 (4)
C7	0.1430 (8)	1.204 (1)	0.671 (1)	3.5 (3)	C43	0.6460 (7)	0.130 (1)	0.679 (1)	3.1 (3)
C8	0.162 (1)	1.293 (1)	0.732 (1)	6.2 (5)	C44	0.6646 (8)	0.101 (1)	0.594 (1)	4.3 (4)
C9	0.192 (1)	1.364 (2)	0.701 (2)	7.7 (6)	C45	0.698 (1)	0.014 (1)	0.567 (1)	6.0 (5)
C10	0.204 (1)	1.340 (1)	0.613 (2)	6.9 (5)	C46	0.709 (1)	−0.040 (1)	0.632 (2)	6.9 (5)
C11	0.190 (1)	1.235 (1)	0.552 (1)	6.4 (5)	C47	0.692 (1)	−0.013 (1)	0.719 (2)	6.7 (5)
C12	0.1574 (9)	1.185 (1)	0.580 (1)	4.7 (4)	C48	0.6565 (9)	0.076 (1)	0.745 (1)	5.3 (4)
C13	0.1305 (8)	1.128 (1)	0.827 (1)	3.8 (4)	C49	0.6244 (8)	0.289 (1)	0.833 (1)	3.0 (3)
C14	0.198 (1)	1.154 (1)	0.873 (2)	6.4 (5)	C50	0.6914 (9)	0.289 (1)	0.883 (1)	4.6 (4)
C15	0.222 (1)	1.155 (2)	0.972 (2)	10.2 (7)	C51	0.711 (1)	0.329 (1)	0.984 (2)	6.6 (5)
C16	0.173 (2)	1.136 (2)	1.020 (2)	10.8 (8)	C52	0.661 (1)	0.372 (2)	1.028 (2)	8.3 (6)
C17	0.104 (1)	1.114 (2)	0.976 (2)	8.1 (6)	C53	0.595 (1)	0.372 (1)	0.979 (2)	6.6 (5)
C18	0.084 (1)	1.106 (1)	0.879 (1)	5.9 (4)	C54	0.5772 (9)	0.335 (1)	0.881 (1)	4.5 (4)
C19	0.1404 (8)	0.699 (1)	0.695 (1)	3.3 (3)	C55	0.6405 (8)	0.641 (1)	0.696 (1)	3.0 (3)
C20	0.1490 (8)	0.729 (1)	0.619 (1)	3.2 (3)	C56	0.6531 (8)	0.572 (1)	0.619 (1)	3.3 (3)
C21	0.2067 (8)	0.705 (1)	0.581 (1)	3.7 (4)	C57	0.7141 (9)	0.579 (1)	0.586 (1)	4.3 (4)
C22	0.2548 (9)	0.648 (1)	0.623 (1)	4.8 (4)	C58	0.7611 (9)	0.653 (1)	0.636 (1)	4.9 (4)
C23	0.246 (1)	0.620 (1)	0.698 (1)	5.7 (4)	C59	0.7512 (9)	0.721 (1)	0.714 (1)	5.3 (4)
C24	0.1895 (9)	0.642 (1)	0.736 (1)	5.0 (4)	C60	0.6917 (9)	0.715 (1)	0.748 (1)	4.4 (4)
C25	0.122 (8)	0.611 (1)	0.693 (1)	3.7 (3)	C61	0.5102 (9)	0.734 (1)	0.695 (1)	3.8 (4)
C26	0.039 (1)	0.531 (2)	0.648 (2)	10.2 (7)	C62	0.5453 (9)	0.804 (1)	0.678 (1)	5.3 (4)
C27	−0.005 (1)	0.444 (2)	0.618 (2)	9.6 (7)	C63	0.503 (1)	0.877 (1)	0.648 (1)	6.3 (5)
C28	−0.068 (1)	0.422 (1)	0.623 (2)	6.4 (5)	C64	0.435 (1)	0.877 (1)	0.641 (1)	6.1 (5)
C29	−0.091 (1)	0.516 (2)	0.677 (2)	9.7 (7)	C65	0.402 (1)	0.803 (1)	0.653 (1)	6.5 (5)
C30	−0.051 (1)	0.605 (2)	0.710 (2)	8.4 (6)	C66	0.442 (1)	0.730 (1)	0.683 (2)	6.8 (5)
C31	0.0822 (8)	0.755 (1)	0.862 (1)	4.1 (4)	C67	0.5788 (9)	0.663 (1)	0.858 (1)	4.4 (4)
C32	0.072 (1)	0.699 (2)	0.917 (2)	9.3 (6)	C68	0.561 (1)	0.745 (2)	0.911 (2)	7.4 (6)
C33	0.094 (1)	0.734 (2)	1.021 (2)	10.3 (7)	C69	0.581 (1)	0.763 (2)	1.016 (2)	9.1 (6)
C34	0.115 (1)	0.819 (2)	1.060 (2)	8.2 (6)	C70	0.611 (1)	0.700 (2)	1.058 (2)	7.6 (6)
C35	0.131 (1)	0.875 (2)	1.013 (2)	9.3 (7)	C71	0.629 (1)	0.619 (2)	1.004 (2)	8.1 (6)
C36	0.113 (1)	0.841 (2)	0.909 (2)	8.9 (6)	C72	0.612 (1)	0.598 (2)	0.901 (2)	7.2 (5)

This folding has been observed in other thiolato-bridged complexes of d^8 metal ions, and in Table VI we compare our structural parameters with those found previously.[13] Compared to the compound $[Pd(S_2CSCMe_3)(\mu\text{-}SCMe_3)]_2$[13a] the Pd–Pd separation is short and the dihedral angles between the planes is small. These differences appear to be more significant than the difference in the S⋯S separations (2.98 Å as compared to 3.088 Å). Indeed the dihedral angle of 77° appears to be very small, and only the chelate complexes of nickel(II) (Table VI) show such a small angle.

The distances and angles in the Pd_2S_2 rhombus are within normal range. The distance Pd–S falls between 2.284 and 2.414 Å. The bridge is unsymmetrical because of the phosphorus and iodine atoms being located at the different positions across from the bridging thiolates. In agreement with trans influence arguments the Pd–S distance trans to the phosphine (2.372–2.414 Å) is slightly longer than the Pd–S distance trans to iodide (2.284–2.308 Å). The distances Pd–P and Pd–I remain constant in the respective ranges 2.224–2.240 and 2.593–2.601 Å. The four angles within the Pd_2S_2 rhombus are all closely similar. Thus the S–Pd–S angle is 78.8° in one molecule and 79.2° in the other, whereas the corresponding values for Pd–S–Pd are 78.5 and 76.3°. This small value for the Pd–S–Pd corresponds with the small folding angle between the palladium planes in each dimer.

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Table V. Bond Distances and Angles for the Two Molecules of $[PdI(o\text{-}SC_6H_4PPh_2)]_2$

molecule 1		molecule 2	
Pd(1)-Pd(2)	2.964 (2)	Pd(3)-Pd(4)	2.916 (2)
Pd(1)-P(1)	2.224 (4)	Pd(3)-P(3)	2.232 (4)
Pd(1)-S(1)	2.284 (4)	Pd(3)-S(3)	2.294 (4)
Pd(1)-S(2)	2.399 (4)	Pd(3)-S(4)	2.414 (4)
Pd(1)-I(1)	2.593 (2)	Pd(3)-I(3)	2.593 (2)
Pd(2)-P(2)	2.237 (4)	Pd(4)-P(4)	2.240 (4)
Pd(2)-S(2)	2.308 (4)	Pd(4)-S(4)	2.312 (4)
Pd(2)-S(1)	2.372 (4)	Pd(4)-S(3)	2.407 (4)
Pd(2)-I(2)	2.600 (2)	Pd(4)-I(4)	2.601 (2)
S(1)-S(2)	2.972 (5)	S(3)-S(4)	3.006 (6)
Ring 1		Ring 1	
P(1)-C(1)	1.84 (2)	P(3)-C(37)	1.83 (2)
S(1)-C(2)	1.76 (1)	S(3)-C(38)	1.80 (1)
C(1)-C(2)	1.36 (2)	C(37)-C(38)	1.38 (2)
C(2)-C(3)	1.41 (2)	C(38)-C(39)	1.37 (2)
C(3)-C(4)	1.42 (2)	C(39)-C(40)	1.39 (2)
C(4)-C(5)	1.42 (2)	C(40)-C(41)	1.40 (2)
C(5)-C(6)	1.40 (2)	C(41)-C(42)	1.39 (2)
C(6)-C(1)	1.38 (2)	C(42)-C(37)	1.39 (2)
Ring 2		Ring 2	
P(1)-C(7)	1.81 (1)	P(3)-C(43)	1.85 (1)
C(7)-C(8)	1.37 (2)	C(43)-C(44)	1.36 (2)
C(8)-C(9)	1.43 (2)	C(44)-C(45)	1.44 (2)
C(9)-C(10)	1.33 (3)	C(45)-C(46)	1.39 (2)
C(10)-C(11)	1.35 (2)	C(46)-C(47)	1.36 (2)
C(11)-C(12)	1.40 (2)	C(47)-C(48)	1.47 (2)
C(12)-C(7)	1.39 (2)	C(48)-C(43)	1.40 (2)
Ring 3		Ring 3	
P(1)-C(13)	1.79 (2)	P(3)-C(49)	1.81 (2)
C(13)-C(14)	1.37 (2)	C(49)-C(50)	1.37 (2)
C(14)-C(15)	1.43 (3)	C(50)-C(51)	1.43 (2)
C(15)-C(16)	1.40 (3)	C(51)-C(52)	1.37 (3)
C(16)-C(17)	1.38 (3)	C(52)-C(53)	1.36 (3)
C(17)-C(18)	1.38 (3)	C(53)-C(54)	1.38 (2)
C(18)-C(13)	1.41 (2)	C(54)-C(49)	1.37 (2)
Ring 4		Ring 4	
P(2)-C(19)	1.82 (2)	P(4)-C(55)	1.82 (1)
S(2)-C(20)	1.76 (2)	S(4)-C(56)	1.76 (2)
C(19)-C(20)	1.36 (2)	C(55)-C(56)	1.38 (2)
C(20)-C(21)	1.39 (2)	C(56)-C(57)	1.42 (2)
C(21)-C(22)	1.41 (2)	C(57)-C(58)	1.38 (2)
C(22)-C(23)	1.34 (2)	C(58)-C(59)	1.37 (2)
C(23)-C(24)	1.37 (2)	C(59)-C(60)	1.40 (2)
C(24)-C(19)	1.42 (2)	C(60)-C(55)	1.43 (2)
Ring 5		Ring 5	
P(2)-C(25)	1.79 (2)	P(4)-C(61)	1.84 (2)
C(25)-C(26)	1.37 (3)	C(61)-C(62)	1.36 (2)
C(26)-C(27)	1.46 (3)	C(62)-C(63)	1.46 (2)
C(27)-C(28)	1.29 (3)	C(63)-C(64)	1.33 (2)
C(28)-C(29)	1.33 (3)	C(64)-C(65)	1.34 (2)
C(29)-C(30)	1.46 (3)	C(65)-C(66)	1.44 (2)
C(30)-C(25)	1.34 (2)	C(66)-C(61)	1.32 (2)
Ring 6		Ring 6	
P(2)-C(31)	1.78 (2)	P(4)-C(67)	1.80 (2)
C(31)-C(32)	1.34 (2)	C(67)-C(68)	1.35 (2)
C(32)-C(33)	1.46 (3)	C(68)-C(69)	1.48 (3)
C(33)-C(34)	1.27 (3)	C(69)-C(70)	1.32 (3)
C(34)-C(35)	1.29 (3)	C(70)-C(71)	1.33 (3)
C(35)-C(36)	1.45 (3)	C(71)-C(72)	1.44 (3)
C(36)-C(31)	1.36 (3)	C(72)-C(67)	1.38 (2)
Angles (Deg)			
P(1)-Pd(1)-S(1)	87.9 (1)	P(3)-Pd(3)-S(3)	88.3 (1)
S(1)-Pd(1)-S(2)	78.7 (1)	S(3)-Pd(3)-S(4)	79.3 (1)
S(2)-Pd(1)-I(1)	99.5 (1)	S(4)-Pd(3)-I(3)	98.8 (1)
I(1)-Pd(1)-P(1)	94.0 (1)	I(3)-Pd(3)-P(3)	93.9 (1)
P(2)-Pd(2)-S(2)	86.8 (1)	P(4)-Pd(4)-S(4)	87.4 (1)
S(2)-Pd(2)-S(1)	78.8 (1)	S(4)-Pd(4)-S(3)	79.1 (1)
S(1)-Pd(2)-I(2)	97.4 (1)	S(3)-Pd(4)-I(4)	97.2 (1)
I(2)-Pd(2)-P(2)	97.1 (1)	I(4)-Pd(4)-P(4)	95.9 (1)
Pd(1)-S(1)-Pd(2)	79.1 (1)	Pd(3)-S(3)-Pd(4)	76.6 (1)
Pd(1)-S(2)-Pd(2)	78.0 (1)	Pd(3)-S(4)-Pd(4)	76.1 (1)
C(1)-P(1)-C(7)	107.3 (7)	C(37)-P(3)-C(43)	107.5 (6)
C(1)-P(1)-C(13)	103.9 (7)	C(37)-P(3)-C(49)	103.0 (7)
C(7)-P(1)-C(13)	107.1 (7)	C(43)-P(3)-C(49)	106.1 (7)
C(19)-P(2)-C(25)	104.4 (7)	C(55)-P(4)-C(61)	105.5 (7)
C(19)-P(2)-C(31)	106.7 (7)	C(55)-P(4)-C(67)	104.9 (7)
C(25)-P(2)-C(31)	108.5 (8)	C(61)-P(4)-C(67)	107.9 (8)
Ring 1		Ring 1	
S(1)-C(2)-C(1)	120 (1)	S(3)-C(38)-C(37)	121 (1)
S(1)-C(2)-C(3)	118 (1)	S(3)-C(38)-C(39)	117 (1)
P(1)-C(1)-C(2)	118 (1)	P(3)-C(37)-C(38)	118 (1)
P(1)-C(1)-C(6)	121 (1)	P(3)-C(37)-C(42)	123 (1)
C(1)-C(2)-C(3)	122 (1)	C(37)-C(38)-C(39)	122 (1)
C(2)-C(3)-C(4)	118 (1)	C(38)-C(39)-C(40)	119 (2)
C(3)-C(4)-C(5)	121 (2)	C(39)-C(40)-C(41)	120 (2)
C(4)-C(5)-C(6)	117 (2)	C(40)-C(41)-C(42)	120 (1)
C(5)-C(6)-C(1)	122 (2)	C(41)-C(42)-C(37)	119 (1)
C(6)-C(1)-C(2)	121 (1)	C(42)-C(37)-C(38)	120 (1)
Ring 2		Ring 2	
P(1)-C(7)-C(8)	124 (1)	P(3)-C(43)-C(44)	118 (1)
P(1)-C(7)-C(12)	117 (1)	P(3)-C(43)-C(48)	119 (1)
C(7)-C(8)-C(9)	120 (2)	C(43)-C(44)-C(45)	121 (2)
C(8)-C(9)-C(10)	118 (2)	C(44)-C(45)-C(46)	117 (2)
C(9)-C(10)-C(11)	124 (2)	C(45)-C(46)-C(47)	122 (2)
C(10)-C(11)-C(12)	118 (2)	C(46)-C(47)-C(48)	121 (2)
C(11)-C(12)-C(7)	121 (2)	C(47)-C(48)-C(43)	116 (2)
C(12)-C(7)-C(8)	119 (2)	C(48)-C(43)-C(44)	122 (1)
Ring 3		Ring 3	
P(1)-C(13)-C(14)	121 (1)	P(3)-C(49)-C(50)	120 (1)
P(1)-C(13)-C(18)	119 (1)	P(3)-C(49)-C(54)	120 (1)
C(13)-C(14)-C(15)	120 (2)	C(49)-C(50)-C(51)	121 (2)
C(14)-C(15)-C(16)	118 (2)	C(50)-C(51)-C(52)	117 (2)
C(15)-C(16)-C(17)	123 (3)	C(51)-C(52)-C(53)	122 (2)
C(16)-C(17)-C(18)	117 (2)	C(52)-C(53)-C(54)	119 (2)
C(17)-C(18)-C(13)	122 (2)	C(53)-C(54)-C(59)	121 (2)
C(18)-C(13)-C(14)	120 (2)	C(54)-C(49)-C(50)	119 (2)
Ring 4		Ring 4	
S(2)-C(20)-C(19)	121 (1)	S(4)-C(56)-C(55)	120 (1)
S(2)-C(20)-C(21)	119 (1)	S(4)-C(56)-C(57)	120 (1)
P(2)-C(19)-C(20)	118 (1)	P(4)-C(55)-C(56)	119 (1)
P(2)-C(19)-C(24)	121 (1)	P(4)-C(55)-C(60)	122 (1)
C(19)-C(20)-C(21)	120 (1)	C(55)-C(56)-C(57)	120 (1)
C(20)-C(21)-C(22)	118 (1)	C(56)-C(57)-C(58)	118 (2)
C(21)-C(22)-C(23)	121 (2)	C(57)-C(58)-C(59)	123 (2)
C(22)-C(23)-C(24)	121 (2)	C(58)-C(59)-C(60)	119 (2)
C(23)-C(24)-C(19)	119 (2)	C(59)-C(60)-C(55)	119 (2)
C(24)-C(19)-C(20)	121 (1)	C(60)-C(55)-C(56)	120 (2)
Ring 5		Ring 5	
P(2)-C(25)-C(26)	123 (2)	P(4)-C(61)-C(62)	119 (1)
P(2)-C(25)-C(30)	119 (1)	P(4)-C(61)-C(66)	118 (1)
C(25)-C(26)-C(27)	118 (2)	C(61)-C(62)-C(63)	116 (2)
C(26)-C(27)-C(28)	122 (2)	C(62)-C(63)-C(64)	122 (2)
C(27)-C(28)-C(29)	120 (2)	C(63)-C(64)-C(65)	119 (2)
C(28)-C(29)-C(30)	119 (2)	C(64)-C(65)-C(66)	120 (2)
C(29)-C(30)-C(25)	121 (2)	C(65)-C(66)-C(61)	120 (2)
C(30)-C(25)-C(26)	118 (2)	C(66)-C(61)-C(62)	122 (2)
Ring 6		Ring 6	
P(2)-C(31)-C(32)	125 (2)	P(4)-C(67)-C(68)	120 (2)
P(2)-C(31)-C(36)	118 (2)	P(4)-C(67)-C(72)	119 (2)
C(31)-C(32)-C(33)	120 (2)	C(67)-C(68)-C(69)	117 (2)
C(32)-C(33)-C(34)	120 (3)	C(68)-C(69)-C(70)	122 (2)
C(33)-C(34)-C(35)	123 (3)	C(69)-C(70)-C(71)	120 (2)
C(34)-C(35)-C(36)	117 (3)	C(70)-C(71)-C(72)	121 (2)
C(35)-C(36)-C(31)	122 (2)	C(71)-C(72)-C(67)	119 (2)
C(36)-C(31)-C(32)	116 (2)	C(72)-C(67)-C(68)	121 (2)

Dihedral Angle (Deg) between Planes: Molecule 1, 74.3; Molecule 2, 79.8

Table VI. Comparative M-M Distances, S-S Distances, and Dihedral Angles between Planes for Thiolato-Bridged Multimetallics of d^8 Ions

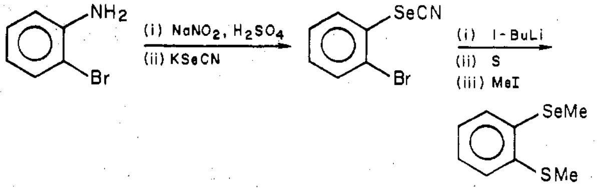
	M-M, A	S-S, A	dihedral angle, deg
$[PdI(o\text{-}SC_6H_4PPh_2)]_2$	2.964	2.98	77
$[Pd(SC_6F_5)(\mu\text{-}SC_6F_5)PPh_3]_2$ [13a,b]	3.54	3.2	
$[Pd(S_2CSCMe_3)(\mu\text{-}SCMe_3)]_2$ [13a]	3.162	3.088	131.8
$[Pd(S(CH_2)_2S(CH_2)_2S)]_3$	3.41-3.66		
$[Rh(SPh)CO(PMe_3)]_2$ [13d]	3.06	3.100	113
$[Ir(SPh)(CO)_2]_2$ [13e]	3.106	2.99	115.2
$[Ir(S\text{-}t\text{-}Bu)(CO)P(OMe)_3]_2$ [13f]	3.216		123.2
$[Ni(S(CH_2)_2S(CH_2)_2S)]_2$ [13g]	2.73		82
$[Ni(S(CH_2)_2)_2P(CH_2)_2SH]_2$ [13a,h]	2.647		
$[Ni_3(S(CH_2)_2NH_2)_4]Cl_2$ [13i]	2.73		78
$[Ni(SEt)_2]_6$ [13a,j]	2.92	~2.92	

The distances and angles in the Pd_2S_2 rhombus show correlation with previous structures. Nevertheless, as expected, the data do not confirm any previous postulates about metal–metal bonding or the origin of the folding about the S–S line. From the shortness of the Pd–Pd interaction and the acute folding angle between the palladium planes it may be expected that some bonding occurs between palladiums. This is not necessarily the case, however, and recent calculations have minimized the significance of metal–metal bonding being a dominant feature in causing an acute folding angle between the metal coordination planes.[14]

Complexes of Ruthenium(II) and of *o*-(Methylseleno)thioanisole. When a solution of $RuCl_3 \cdot xH_2O$ and *o*-(diphenylphosphino)thioanisole is refluxed for 12 h, the ruthenium(II) complex $RuCl_2(o\text{-}Ph_2PC_6H_4SMe)_2$ is formed in high yield. The complex is yellow which contrasts with the red color of the compound $RuCl_2(o\text{-}Ph_2PC_6H_4OMe)_2$.[10] The compound shows a single stretch band in the far-IR spectrum at 336 cm^{-1} due to ν(Ru–Cl) which is indicative of mutually trans chlorides. The stereochemical arrangement of the *o*-(diphenylphosphino)thioanisole ligand about the ruthenium(II) has not been determined. An X-ray structure of the compound $RuCl_2(o\text{-}Ph_2PC_6H_4OMe)_2$ shows a trans arrangement of chlorides and a cis stereochemistry for the coordinated phosphines and ethers.[15] The observance of single resonances at δ 1.90 (^1H) and 60.4 (^{31}P) confirms the presence of a single isomer. Reaction times of only 4 h do nevertheless lead to products containing a mixture of isomers. The second isomer shows a methyl resonance at δ 1.20. This isomer converts to the thermodynamic one on further heating in ethanol solvent.

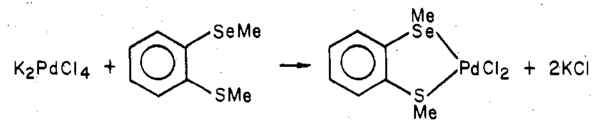
Using a similar experimental procedure, except that the reaction is carried out at ambient temperature, we have prepared the selenium analogue $RuCl_2(o\text{-}Ph_2PC_6H_4SeMe)_2$. Refluxing the reaction mixture leads to a yellow product which is insoluble in common organic solvents. In view of the more facile demethylation from a coordinated selenoether than from a thioether, it is likely this product is a selenolato polymer of ruthenium. The ambient-temperature product is cream colored and is slightly soluble in chloroform.

The compound *o*-(methylseleno)thioanisole has been prepared by using a previously described experimental procedure (eq 4).[16] The ^1H NMR spectrum shows two methyl resonances centered at δ 2.38 and 2.22. The upfield peak is assigned as the SeMe resonance from the observation of ^{77}Se (7.5% abundance) satellites on this peak. From the satellite separation we obtain $^2J(^1H\text{-}^{77}Se)$ = 13 Hz. The ^{13}C NMR spectrum shows two resonances centered at δ 7.3 and 15.8. The peak at δ 7.3 is again assigned as the SeMe resonance on account of coupling to ^{77}Se ($^1J(^{13}C\text{-}^{77}Se)$ = 64 Hz). The ^{77}Se NMR spectrum shows a quartet resonance centered at a Larmor frequency of 17 172 125 Hz.[17] The quartet separation of 12 Hz confirms this and is caused by the coupling $^2J(^{77}Se\text{-}^1H)$ to the methyl group. Spin decoupling collapses the quartet to a singlet in the $^{77}Se\{^1H\}$ spectrum.



(4)

The compound *o*-(methylseleno)thioanisole reacts rapidly with potassium tetrachloropalladate(II) to give the yellow compound dichloro[*o*-(methylseleno)thioanisole]palladium(II) (eq 5). This complex is the first one to be prepared from *o*-(methylseleno)thioanisole. The far-infrared spectrum shows bands at 320 and 300 cm^{-1} which is to be expected for the cis geometry of the chlorides. The compound is insoluble in common organic solvents but can be dissolved in trifluoroacetic acid. An ^1H NMR spectrum in this solvent shows peaks for the methyl resonance at δ 2.61 (SMe) and 2.53 (SeMe). The ^{13}C NMR spectrum has resonances in the methyl carbon region at δ 22.7 (SeMe) and 29.4 (SMe).



(5)

Experimental Section

The compounds *o*-(diphenylphosphino)thioanisole (PSMe), *o*-(diphenylphosphino)selenoanisole (PSeMe), *o*-(diphenylphosphino)anisole (PO), and (*o*-diphenylphosphino)-*N*,*N*-dimethylaniline (PN) and complexes $PdI_2(PSMe)$, [PdI(*o*-(diphenylphosphino)benzenethiolato)]$_2$, $Pt(SMe)_2(PPh_3)_2$, $[Pt(PN)_2](ClO_4)_2$, $PdCl_2(PN)$, $[RhCl_2(PN)_2]SbF_6$, and $RuCl_2(PO)_2$ were prepared by published methods. The syntheses of $Pd(SCN)_2(PSMe)$ and $Pd(SCN)_2(PSeMe)$ followed published procedures. Sodium tetrachloropalladate(II) and ruthenium trichloride hydrate were purchased from Engelhard or Mathey Bishop, Inc. The compounds MeSCN and MeNCS were commercial samples.

^1H NMR spectra were measured on a JEOL MH100 NMR spectrometer as solutions in $CDCl_3$ using Me_4Si as internal reference. ^{13}C, ^{31}P, and ^{77}Se NMR spectra were measured on a Bruker WH90 NMR spectrometer. The ^{77}Se resonance was located from published shift positions of similar compounds.[17] The resonance is measured by using a deuterium lock signal from $CDCl_3$. ^{13}C spectra were obtained as solutions in $CDCl_3$ or CD_3CN by using tetramethylsilane as external reference. ^{31}P spectra were obtained in $CDCl_3$ solution by using 85% H_3PO_4 as external reference. Electronic spectra were measured on a Cary 14 spectrophotometer. Solutions were made in acetonitrile solvent and measured in 1-cm matched cells. Infrared spectra were measured as Nujol mulls on a Perkin-Elmer Model 700 spectrometer. Far-infrared spectra were measured as Vaseline mulls on a polyethylene plate by using a Hitachi Perkin-Elmer Model FIS-3 spectrometer. Microanalyses were carried out by Galbraith, Inc., Knoxville, TN, or by Canadian Microanalytical Service Ltd., Vancouver, British Columbia, Canada.

Dichlorobis[*o*-(diphenylphosphino)thioanisole]ruthenium(II). A solution containing $o\text{-}Ph_2PC_6H_4SMe$ (477.7 mg) in ethanol (50 mL) was heated to boiling. To this hot solution was added $RuCl_3 \cdot xH_2O$ (108.5 mg, 39% Ru) dissolved in ethanol (5 mL). Within 2–3 min the solution changed from brown to green-yellow, and a precipitate began to form. The mixture was refluxed for 12 h under a nitrogen atmosphere. After the mixture was cooled to room temperature the

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(14) (a) Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 7240. (b) Norman, J. G.; Gmur, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 1446.

(15) Jeffrey, J. C.; Rauchfuss, T. B. *Inorg. Chem.* **1979**, *18*, 2658.

(16) Pierpont, C. Ph.D. Thesis, Brown University, 1972.

(17) This frequency is measured against an external D_2O lock signal at 13 819 263 Hz. The instrument settings were obtained from: Pan, W.-H.; Fackler, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 5783.

yellow precipitate was filtered, washed sequentially with ethanol and diethyl ether, and dried in vacuo. Refluxing the mixture for 4 h gives a yellow product which shows two resonances (ratio 2:1) in the ^{1}H NMR spectrum of δ 1.90 and 1.20. Refluxing this material in ethanol (under nitrogen) for further 8 h gives pure material (δ 1.90). This is apparently a second isomer which converts to the thermodynamic one under prolonged reaction. The yield was 312.5 mg (95%). Anal. Calcd for $C_{38}H_{34}Cl_2P_2RuS_2$: C, 57.9; H, 4.35; Cl, 9.00. Found: C, 57.4; H, 4.56; Cl, 10.2. ν(Ru–Cl) 336 cm^{-1}. $\delta(^1H)$ 1.90 (Me); $\delta(^{31}P)$ 60.8.

***o*-(Methylseleno)thioanisole.** *o*-(Bromoseleno)anisole (9.67 g), prepared as described previously,[16] was dissolved in a mixture of hexane and diethyl ether (50 mL of each) and treated with *n*-butyllithium (11.64 mL of a 3.33 M solution) under nitrogen with vigorous stirring. The mixture was stirred for an additional 30 min, and then elemental sulfur (1.24 g) was added slowly over a period of 30 min. Then methyl iodide (10 mL, 22.8 g) was added slowly and the mixture allowed to warm to room temperature. The mixture was hydrolyzed with water (60 mL). All solid material dissolved, and the pale yellow organic layer was separated, washed with water, dried over magnesium sulfate, and concentrated to an oil. The product was distilled and the fraction at 78 °C (0.5 mm) collected. $\delta(^1H)$ 2.38 (SMe), 2.22 (SeMe).

Dichloro[*o*-(methylseleno)thioanisole]palladium(II). A solution of *o*-(methylseleno)thioanisole (77.3 mg) in acetone (5 mL) was heated to boiling. To this solution was added a solution of K_2PdCl_4 (102.1 mg) in water (7 mL). An orange precipitate formed. The mixture was stirred for 10 min and the yellow complex filtered, washed sequentially with acetone, methanol, and diethyl ether, and dried in vacuo. The yield was 108.1 mg (88%). Anal. Calcd for $C_8H_{10}Cl_2PdSeS$: C, 24.4; H, 2.56. Found: C, 24.3; H, 2.39. $\delta(^1H)$ 2.61 (SMe), 2.53 (SeMe). The complex is insoluble in common organic solvents but is soluble in CF_3CO_2H. ν(Pd–Cl) 320, 300 cm^{-1}.

Bis(thiocyanato)[*o*-(diphenylphosphino)thioanisole]palladium(II). A solution containing *o*-(diphenylphosphino)thioanisole (545 mg) and sodium thiocyanate (1.202 g) in ethanol (25 mL) was heated to 50 °C. Potassium tetrachloropalladate(II) (519 mg) in water (25 mL) was added, and a yellow precipitate formed. After being stirred for 15 min at 50 °C, the mixture was allowed to cool to room temperature. The complex was filtered, washed sequentially with ethanol and diethyl ether, and dried in vacuo. The yield was 654 mg (77%). Anal. Calcd for $C_{21}H_{17}N_2PdPS_3$: C, 47.5; H, 3.23. Found: C, 47.4; H, 3.32.

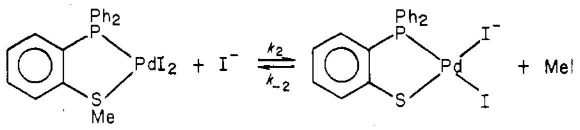
Bis(thiocyanato)[*o*-(diphenylphosphino)selenoanisole]palladium(II). To a solution containing sodium tetrachloropalladate(II) (504 mg) and sodium thiocyanate (557 mg) in ethanol (50 mL) was added a solution of *o*-(diphenylphosphino)selenoanisole (618 mg) in acetone (10 mL). The mixture was stirred for 1 h as a yellow precipitate formed. The complex was recrystallized from CH_2Cl_2/EtOH and dried in vacuo. The yield was 736 mg (74%). Anal. Calcd for $C_{21}H_{17}N_2PdPSeS_2$: C, 43.7; H, 2.97. Found: C, 43.5; H, 3.00.

Dichlorobis[*o*-(diphenylphosphino)selenoanisole]ruthenium(II). With use of a similar procedure as for dichloro[*o*-(diphenylphosphino)thioanisole]ruthenium with *o*-$Ph_2PC_6H_4SeMe$ (138 mg) in ethanol (10 mL) and $RuCl_3 \cdot xH_2O$ (32 mg) in ethanol (3 mL) at *room temperature*, the compound was obtained as an off-white solid. The yield was 64 mg (59%). The compound is slightly soluble in CH_2Cl_2; mp 270 °C dec. Anal. Calcd for $C_{38}H_{34}Cl_2P_2RuSe_2$: C, 51.7; H, 3.88. Found: C, 51.0; H, 3.83. ν(Ru–Cl) 330 cm^{-1}.

Kinetic Measurements

Rate measurements were made by measuring the decrease in the thiomethyl or selenomethyl signal in the ^{1}H NMR spectrum. The peak profile allowed height to be used as a direct measure of concentration. A base line method was used to measure peak height, the average resulting from several scans across the resonance. The peak heights were compared to the initial peak height and ln (PH_t/PH_0) (PH_0 and PH_t are initial and intermediate time to peak heights, respectively) plotted against time in seconds. For the thiocyanate data the plots were linear for two half-lives. All kinetic runs were made under pseudo-first-order conditions where the initial concentration ratio of nucleophile to compounds was not less than 10:1. The solutions were made by dissolving the reactants in 0.4 mL of CD_3CN and transferring the solution to a 5-mm NMR tube by using a syringe. The tube was flushed with nitrogen and capped before immersing the solution in a constant temperature bath. For the complex $Pd(SCN)_2(o\text{-}MeSeC_6H_4PPh_2)$, a separate solution in CH_2Cl_2 (0.1 mL) was mixed with a solution of NaSCN in CD_3CN (0.3 mL). The mixed solution was then transferred to the NMR tube as before. Time was measured 15 s after insertion of the NMR tube in the bath and continued for 15 s after ice-water quenching. The constant-temperature bath was maintained by use of a mercury switch and control box. Temperatures were accurate to ±0.3 °C of the given temperature.

For the nucleophile thiocyanate the reaction can also be followed by measuring the peak height of the MeSCN resonance. For the iodide work a known quantity of anisole was added to the solution as a check on signal-height stability over the time of the run. For the iodide data a plot of ln (PH_t/PH_0) against time was not linear, and hence k(obsd) could not be obtained from this plot. Instead a plot was made of concentration against time, and from the graph an estimate of rate was made after 20% and 30% completion of reaction by measuring the tangent to the plot at that particular concentration. With use of the four iodide concentrations 0.088, 0.15, 0.21, and 0.27 M, eight equations were created which can be solved for k_2 and k_{-2}. In practice only seven values were realizable because equilibrium was reached before 30% demethylation when the iodide concentration was 0.88 M. (See eq 6.) These values allowed an estimate of the equilibrium



(6)

constant K for the reaction, and the validity of this measured value checked by separately estimating the equilibrium concentration of $PdI_2(o\text{-}MeSC_6H_4PPh_2)$ in a closed system. Respective values of k_2, k_{-2}, and K were 3.4×10^{-3} M^{-1} s^{-1}, 0.248 M^{-1} s^{-1}, and 1.37×10^{-2} s^{-1} (77 °C).

Crystal Structure Data

Collection of Data. A single piece of an arrowhead-shaped crystal was cut from a larger crystal. Lengths 0.164, 0.127, and 0.291 mm were measured along the faces of the crystal. The crystal was mounted on a glass fiber. Oscillation and zero-order Weissenberg photographs showed no mirror symmetry. Two axes were readily found, but the third axis of the triclinic cell could not be easily located. The cell matrix was located by using a combination of BLIND and manual methods. The final lattice constants were determined from least-squares refinement of the reciprocal lattice coordinates of 12 accurately centered reflections ($\lambda_{Mo\,K\alpha} = 0.71069$ Å) and are $a = 19.870$ (6) Å, $b = 14.754$ (5) Å, $c = 14.856$ (6) Å, $\cos \alpha = -0.2643$ (6), $\cos \beta = -0.2226$ (4), and $\cos \gamma = 0.0089$ (4). The calculated density for 4 formula units per unit cell is 1.71 g/cm^3. The crystal belongs to the space group $P\bar{1}$.

Intensity data were collected on an automated Picker full-circle diffractometer with Zr-filtered Mo Kα radiation. A total of 9181 unique reflections were collected in the range $4° \le 2\theta \le 42°$ with use of a θ–2θ scan with a scan width of 1.8° with 20 steps/deg and 3.5 s/step. The reflections $4° \le 2\theta \le 15°$ and $15° \le 2\theta \le 42°$ were collected with two separate filters of approximate transmission ratio 2.50:1. Of the 9181 reflections, 6149 were regarded as "observed", i.e., with $I \ge 3\sigma(I)$. The standard deviation of each reflection was calculated by $\sigma^2(I) = TC + BG + 0.03^2I^2$, where TC is total counts, BG is background counts, and $I = TC - BG$. The background count was 21 s. The intensities of three reflections were monitored every 40 reflections to check for decomposition, etc. These intensities decreased by approximately 5% during data collection, and a decay correction was applied to the data by using the DIFFDAT program before proceeding with further data treatment.

Structure Solution and Refinement. Data were corrected for absorption ($\mu = 25.87$ cm^{-1}; transmission factors ranged from 0.70 to 0.77), and the positions of the Pd and I atoms were obtained from MULTAN. Imprecise positions for the P and S atoms were evident from MULTAN. The atomic coordinates for these and the carbon atoms were found by using Fourier mapping techniques on the 3σ data set. Initially all nonhydrogen parameters were refined isotropically. Subsequently the Pd, I, S, and P atoms were refined anisotropically. At this stage of refinement, all nonhydrogen parameters converged to an $R = \sum||F_o| - |F_c||/\sum|F_o|$ of 0.073 and an $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$ of 0.073. Fourier difference maps revealed the presence of diethyl ether molecules in the lattice. The molecules were too distant from either palladium dimer to interact, and there was one diethyl ether molecule for each palladium dimer in the cell. Refinement was continued including the nonhydrogen atoms from these diethyl ether molecules and the hydrogen atoms of the palladium dimers.[18] Refinement converged to $R = 0.062$ and $R_w = 0.056$.

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Registry No. *o*-$MeSC_6H_4PPh_2$, 14791-94-7; $Pd(SCN)_2$(*o*-$MeSC_6H_4PPh_2$), 30482-42-9; PdI_2(*o*-$MeSC_6H_4PPh_2$), 28647-06-5; $Pt(SMe)_2(PPh_3)_2$, 56213-50-4; $RuCl_2$(*o*-$MeSC_6H_4PPh_2)_2$, 74449-46-0; *o*-$MeSeC_6H_4PPh_2$, 16566-17-9; $Pd(SCN)_2$(*o*-$MeSeC_6H_4PPh_2$), 30482-43-0; *o*-$MeSeC_6H_4SMe$, 74449-35-7; $PdCl_2$(*o*-$MeSeC_6H_4SMe$), 74449-47-1; $PdCl_2$(*o*-$Me_2NC_6H_4PPh_2$), 14552-56-8; [PdI(*o*-$SC_6H_4PPh_2$)]$_2$, 52543-13-2; [PdI_2(*o*-$SC_6H_4PPh_2$)]$^-$, 71763-87-6; SCN^-, 302-04-5; I^-, 20461-54-5; *o*-$BrSeC_6H_4SMe$, 74449-36-8; K_2PdCl_4, 10025-99-7; Na_2PdCl_4, 10026-00-3; $RuCl_2$(*o*-$MeSeC_6H_4PPh_2)_2$, 74465-44-4.

Supplementary Material Available: A listing of observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page.

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[18] The hydrogen positions were calculated by using the HYDRA program.

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Structure of (η^6-Mesitylene)bis(pentafluorophenyl)nickel(II). Analysis of the Bonding in Arene–ML_2 Complexes

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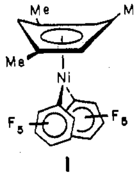
The compound (η^6-mesitylene)bis(pentafluorophenyl)nickel(II) crystallizes in space group $P2_1/n$ with lattice constants of $a = 8.556$ (1) Å, $b = 19.125$ (3) Å, $c = 12.135$ (3) Å, and $\beta = 86.60$ (2)°. The structure was determined from 3279 observed data in the range $(\sin\theta)/\lambda \leq 0.648$ Å^{-1}. The average Ni–C_6F_5 bond distance was 1.898 (4) Å, and the average Ni–C_π bond distance was 2.211 (4) Å. A small "boat" type deformation of the carbon framework in the η^6-mesitylene ligand is observed. Extended Hückel calculations on molecules of the type (benzene)ML_2 reveal that the M–arene distance and deformation of the arene from planarity vary in a predictable manner as a function of the electron count. The 16-electron complexes remain planar and have shorter M–arene distances compared to the 18-electron analogues. This analysis is extended to (arene)ML_4 and other species.

Introduction

Previously we reported[2,3] the synthesis and structures of (π-tol)$M(C_6F_5)_2$ complexes where M = Co(II) and Ni(II). An interesting feature of these molecules is that the π-arene ligand is extremely labile. For example, the solution data indicates that the arene rapidly undergoes exchange at room temperature, with the more electron-releasing arenes being preferred. Other arene complexes normally require much more forcing conditions or a catalyst.[4] Herein we report the structure of the π-mesitylene complex of $(C_6F_5)_2Ni$ (**1**) to establish the structural changes that occur when the more electron-releasing mesitylene is substituted for toluene and also to provide more structural data on complexes of this type. Moreover, we wish to develop an understanding of the bonding in arene–ML_2 complexes. Of particular interest is the fact that the π-arene ligand is sometimes nonplanar. This is, of course, the case for η^4 and η^2 complexes.[5] However, we have observed[3b] that the complex (π-tol)$Ni(C_6F_5)_2$ contains a nonplanar ring which has also been observed in other[6] 18-electron η^6 complexes. The sense of the distortion is that C_1 and C_4 in **2** move away from the metal towards a boat-shaped structure **3**. The distortion is small and exaggerated in **3**; nonetheless it is a definite feature. On the other hand, the 17-electron complex (π-tol)$Co(C_6F_5)_2$ contains a planar η^6-arene ligand.[3b] A preliminary theoretical discussion of this



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