Addition−Elimination Equilibria Involving 16e⁻ Platinum(0) and 18e⁻ Platinum(II) Complexes

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Received April 4, 1996[⊗]

The addition−elimination equilibrium involving a platinum(0) nucleophile [Pt(*N*,*N*′-chelate)(olefin)] (**1**), an organometal electrophile R_mMX_n (M = Hg, Sn; X = Cl, Br, I; R = hydrocarbyl group), and the corresponding five-coordinate adduct [PtX(MR_mX_{n-1})(*N*,*N*′-chelate)(olefin)] (**2**) has been investigated. The influence on the equilibrium of the groups bonded to the electrophilic center and of the ligands bonded to platinum has been evaluated. It has been found that the adduct is stabilized by the presence of electron-donor olefins on platinum and of electron-withdrawing groups on the electrophilic metal. It has also been found that the influence of the halide moving onto platinum can be rationalized in terms of the relative softness of the two metals involved in the equilibrium. The X-ray molecular structures of [Pt(dmphen)(*E*-$MeO_2CCH{=}CHCO_2Me$)] (**1k**, dmphen = 2,9-Me_2-1,10-phenanthroline) and of the related addition product [PtCl($SnMe_2Cl$)(dmphen)(*E*-$MeO_2CCH{=}CHCO_2Me$)] (**2i**) have been determined for a better understanding of the influence of steric and bonding features.

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Published on September 17, 1996 on http://pubs.acs.org | doi: 10.1021/om960268s

Introduction

In the chemistry of transition metal complexes it is generally observed that one of the two reacting systems involved in an oxidative addition/reductive elimination equilibrium is by far more favored. Moreover, the establishment of an equilibrium allowing significant concentrations of all reactants ("reversible" equilibrium) is prevented in many cases by the occurrence of different processes, such as ligand loss,[1] insertion,[2] and competing elimination.[3] As a consequence, the chances of analyzing the influence of relevant factors in a wide range of variation on the same equilibrium are rare. In fact, only through the reactions of Vaska type compounds in iridium chemistry was it possible to carry out a thorough investigation.[4] On the other hand, during a study of oxidative addition to substrates of the type [Pt(*N*,*N*′-chelate)(olefin)] (**1**) to give 18e⁻ five-coordinate adducts (**2**) it was recently found[5] that the reaction can produce a fairly balanced equilibrium provided that a suitable halostannane is the reacting electrophile, as exemplified in eq 1.

$$[Pt(dmphen)(E\text{-}MeO_2CCH{=}CHCO_2Me)] + Me_2SnCl_2 = [PtCl(SnMe_2Cl)(dmphen)(E\text{-}MeO_2CCH{=}CHCO_2Me)] \quad (1)$$

dmphen = 2,9-dimethyl-1,10-phenanthroline

We felt that the study of equilibria concerning oxidative additions to type **1** complexes to give stable adducts deserved further attention for several reasons. (i) Reactions analogous to (1) are to date the only widely effective oxidative processes which afford stable 18e⁻ M(II) adducts from M(0) precursors in the platinum group.[6] (ii) Compounds **1** undergo oxidative addition by a variety of electrophiles.[6] (iii) The electronic and steric features of the coordination environment of **1** can vary within fairly wide ranges. (iv) "Reversible" oxidation/reduction equilibria involving Pt(II) and Pt(IV) species related respectively to **1** and **2** are known:[7] thus, results concerning type (1) reactions allow comparisons in the range of three oxidation states of the same element.

We have extended the preliminary study and assessed that at least one other type of electrophile, i.e. an

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⊗ Abstract published in *Advance ACS Abstracts*, August 1, 1996.

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S0276-7333(96)00268-3 CCC: $12.00 © 1996 American Chemical Society

organomercury halide,[8] can be involved in a reversible addition to **1**, by the activation of a metal−halogen bond, according to the following example in (2).

$$[Pt(dmphen)(Z\text{-}MeO_2CCH{=}CHCO_2Me)] + MeHgCl = [PtCl(HgMe)(dmphen)(Z\text{-}MeO_2CCH{=}CHCO_2Me)] \quad (2)$$

Here we report the results concerning the influence of electronic and steric factors on type (1) and (2) addition/elimination equilibria. In previous literature these factors have been discussed for addition/elimination reactions more often in terms of kinetic influence than with regard to the thermodynamic behavior.[4a]

The X-ray molecular structures of a Pt(II) adduct and of its Pt(0) precursor are also discussed.

Results and Discussion

Table 1 lists the characterization data for new compounds **1** and **2** prepared during this work. The *N*,*N*′-chelate ligands (Figure 1) exhibit a variable degree of rigidity and of in-plane hindrance next to the N atoms. These features are of utmost importance in order to stabilize the five-coordinate species [Pt(X)(Y)(*N*,*N*′-chelate)(olefin)] against olefin release.[6] Although there may be a large variety of functional groups in the coordinated olefin,[6] it is worth noting that a fairly restricted choice of these groups must be made if measurable equilibrium constants are required (see below).

Data concerning the oxidation/elimination processes are reported in Table 2. The rapidly attained equilibrium systems were examined in deuteriochloroform or deuteriotetrachloroethane in order to calculate the equilibrium constants by integrating suitably separated peaks in the ^{1}H NMR spectra. For example, the signals of the methyl groups on the chelating ligands in the five-coordinate adducts are well separated from the corresponding signals in the parent three-coordinate precursors. Alternatively, suitable peaks are those of the olefin protons and/or of the methyl groups on tin. In all cases a metal−halogen bond of the electrophile is broken and the general reaction scheme (3) holds true.

$$[Pt(N,N'\text{-chelate})(olefin)] + R_mMX_n = [PtX(MR_mX_{n-1})(N,N'\text{-chelate})(olefin)] \quad (3)$$

$$M = Hg,\ m = n = 1;\ M = Sn,\ m + n = 4$$

The features of the compounds involved which are relevant in determining the equilibrium position are discussed below.

Substituents in the Olefin Ligand. It is worth discussing the influence on the equilibrium of at least three features of the groups attached to the unsaturated carbons, namely, the following: (i) the electron donor/withdrawing ability; (ii) the steric hindrance; (iii) possible interactions with other ligands.

It is expected that good electron-withdrawing ability stabilizes the electron-rich Pt(0) species. While it was clearly stated[9] that the same feature protects the adduct against olefin release, it should be noted that the formal oxidation involving platinum may be contrasted by the presence of strongly π-acceptor olefins. Thus, it is reasonable that electron-withdrawing substituents hinder the addition.[10]

Steric hindrance should destabilize both the substrate and the adduct. Considering the higher crowding in the latter, it is expected that the stability of the adduct will be reduced much more than that of the trigonal substrate due to the presence of bulky substituents, and therefore this factor should hold back the addition. A parallel kinetic behavior of a similar type was noted in several cases.[11]

In the range of the investigated olefins attractive interactions may involve the axial ligands in the adduct (see below) and act as a stabilization factor, but this should not be significant in the trigonal compound. Thus, factor (iii) should favor the addition. Once again, the previous observations on nonbonded interactions dealt mainly with kinetic effects.[12]

Earlier results concerning the addition of C−X bonds to species **1** in reactions analogous to (3) showed that the presence of electron-withdrawing substituents on unsaturated carbons hinders the addition to type **1** compounds.[13] However, no "reversible" addition/elimination equilibrium was observed and kinetic factors may be responsible for the observed behavior.

The influence of electronic effects (i) is clearly shown by the reaction of the same organotin halide, i.e. Me_2SnCl_2, with the dmphen type **1** compounds derivatives containing, respectively, propene and ethylene or an electron-withdrawing olefin. No evidence of dissociation of the adducts is detected with the two former olefins. The same behavior is observed when only one electron-withdrawing substituent (CN, CO_2Me) is present. A reversible equilibrium occurs when two groups with good withdrawing ability (Cl, CO_2R, COPh) lie on the C=C bond. When two very strong acceptor groups are present, no measurable concentration of the adduct is detected.

The values of the equilibrium constants in Table 2 confirm that a greater donor ability of the olefin is accompanied by a greater stability of the adduct. This conclusion is substantiated by the values measured for the derivatives of *p*-substituted fumarate phenyl esters (**2p**−**r**). In this case, there should be no significant variations of factors (ii) and (iii).

A comparison of the addition constants concerning fumarate alkyl esters derivatives shows that the five-coordinate adducts of the more bulky fumarates are comparatively more stable. Moreover, it is noted that the ratio between the addition constants of the same electrophile, i.e. Me_2SnCl_2, to two type **1** compounds with different fumarates is equal to the ratio of the constants $K_{R/R'}$ pertaining to the exchange schematized by eq 4.

Thus, a unitary value is inferred for the equilibrium constant for the exchange analogous to (4) but involving the five-coordinate adducts. Independent measurements of the constants for this exchange confirm that

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Published on September 17, 1996 on http://pubs.acs.org | doi: 10.1021/om960268s

Table 1. Selected ^{1}H NMR Data[a] [δ (ppm), J (Hz)] for the New Type 1 and 2 Complexes

no.	complex	Sn− or Hg−Me	H(olefin)[b]	Me(chelate)	other selected signals[c]
1a	[Pt(dmphen)(*E*-(PhCOCH=CHCOPh)]		5.14 (82, s, 2H)	2.74 (s, 6H)	
1b	[Pt(dmphen){*E*-(*i*-Pr)O_2CCH=CHCO_2(*i*-Pr)}]		3.76 (88, s, 2H)	3.24 (s, 6H)	5.02 (h, Me_2*CH*O, 2H), 1.28 (d, *Me*$_2$CHO, 3H), 1.24 (d, *Me*$_2$CHO, 3H)
1c	[Pt(dmphen){*E*-(*t*-Bu)O_2CCH=CHCO_2(*t*-Bu)}]		3.67 (88, s, 2H)	3.19 (s, 6H)	1.48 (*t*-BuO, s, 18H)
1d	[Pt(dmphen)(*E*-PhO_2CCH=CHCO_2Ph)][d]		3.95 (87, s, 2H)	3.35 (s, 6H)	
1e	[Pt(dmphen)(*E*-(*p*-ClPh)O_2CCH=CHCO_2(*p*-ClPh)][d]		3.91 (83, s, 2H)	3.31 (s, 6H)	
1f	[Pt(dmphen){*E*-(*p*-MePh)O_2CCH=CHCO_2(*p*-MePh)}][d]		3.91 (84, s, 2H)	3.32 (s, 6H)	2.34 (s, Me, 3H)
1g	[Pt(pimpy)(*E*-MeO_2CCH=CHCO_2Me)]		3.81 (88, d, 1H), 3.64 (90, d, 1H)	2.99 (s, 3H)	9.32 (51, s, N=CH), 3.63 (s, MeO, 3H), 3.38 (s, MeO, 3H)
1h	[Pt(pimpy)(*E*-EtO_2CCH=CHCO_2Et)]		3.75 (90, ABq, 1H)	3.01 (s, 3H)	9.35 (50, s, N=CH, 1H), 1.28 (s, Me*CH*$_2$O, 2H), 1.02 (s, Me*CH*$_2$O, 2H)
1i	[Pt(pimpy){*E*-(*i*-Pr)O_2CCH=CHCO_2(*i*-Pr)}]		3.76 (90, ABq, 2H)	3.04 (s, 3H)	9.34 (50, s, N=CH, 1H), 5.03 (h, Me_2*CH*O, 1H), 4.76 (h, Me_2*CH*O, 1H), 1.28 (d, *Me*$_2$CHO, 3H), 1.24 (d, *Me*$_2$CHO, 3H), 1.11 (d, *Me*$_2$CHO, 3H), 0.68 (d, *Me*$_2$CHO, 3H)
1j	[Pt(pimpy){*E*-(*t*-Bu)O_2CCH=CHCO_2(*t*-Bu)}]		3.67 (91, ABq, 2H)	3.09 (s, 3H)	9.32 (49, s, N=CH, 1H), 1.46 (s, *t*-BuO, 9H), 1.14 (s, *t*-BuO, 9H)
2a	[PtCl(SnMe_2Cl)(dmphen)(CH_2=CHCO_2Me)]	0.79 (s, 3H), 0.20 (s, 3H)	3.63 (*e*, d, 1H), 3.39 (*e*, d, 1H), 3.00 (*e*, d, 1H)	3.36 (s, 3H), 3.20 (s, 3H)	3.81 (s, MeO, 3H)
2b	[PtBr(SnMe_3)(dmphen)(CH_2=CHCN)]	−0.50 (s, 9H)	3.68 (87, t, 1H), 2.88([e],m,2H)	3.42 (s, 3H), 3.27(s,3H)	
2c	[PtI(SnMe_3)(dmphen)(CH_2=CHCN)]	−0.53 (s, 9H)	3.89 (89, t, 1H), 2.92 ([e], dd, 1H), 1H[f]	3.43 (s, 3H), 3.28 (s, 3H)	
2d	[PtCl(SnMe_2Cl)(dmphen)(CH_2=CHCN)]	0.69 (s, 3H), 0.18 (s, 3H)	3.52 (81, t, 1H), 3.23 (*e*, dd, 1H), 3.11 (*e*, dd, 1H)	3.43 (s, 3H), 3.30 (s, 3H)	
2e	[PtCl(SnMe_2Cl)(dmphen)(*E*-ClCH=CHCl)]	0.69 (s, 3H), 0.13 (s, 3H)	5.28 (77, d, 1H), 5.00 (*e*, d, 1H)	3.45 (s, 3H), 3.41 (s, 3H)	
2f	[PtCl(SnMe_2Cl)(dmphen)(*E*-PhOCCH=CHCOPh)]	0.98 (s, 3H), 0.15 (s, 3H)	5.64 (61, d, 1H), 5.40 (64, d, 1H)	2.93 (s, 3H), 2.71 (s, 3H)	
2g	[PtCl(SnPh_2Cl)(dmphen)(*E*-PhOCCH=CHCOPh)]		5.70 (61, d, 1H), 5.36 (64, d, 1H)	2.65 (s, 3H), 2.51 (s, 3H)	
2h	[PtCl(SnMe_2Cl)(dmphen){*Z*-(*t*-Bu)O_2CCH=CHCO_2(*t*-Bu)}]	0.32 (s, 6H)	4.29 (80, s, 2H)	3.32 (s, 6H)	1.53 (s, *t*-BuO, 18H)
2i	[PtCl(SnMe_2Cl)(dmphen)(*E*-MeO_2CCH=CHCO_2Me)]	0.90 (s, 3H), 0.19 (s, 3H)	4.24 (80, ABq, 2H)	3.50 (s, 3H), 3.15 (s, 3H)	3.82 (s, MeO, 3H), 3.76 (s, MeO, 3H)
2j	[PtCl(SnMePhCl)(dmphen)(*E*-MeO_2CCH=CHCO_2Me)] (isomer, 70% abundance)	1.07 (s, 3H)	4.45 (70, d, 1H), 4.15 (71, d, 1H)	3.57 (s, 3H), 2.56 (s, 3H)	3.79 (s, MeO, 3H), 3.78 (s, MeO, 3H)
2k	[PtCl(SnMe_2Cl)(dmphen)(*E*-EtO_2CCH=CHCO_2Et)]	0.88 (s, 3H), 0.19 (s, 3H)	2H[f]	3.50 (s, 3H), 3.17 (s, 3H)	
2l	[PtCl(SnMePhCl)(dmphen)(*E*-EtO_2CCH=CHCO_2Et)] (isomer, 70% abundance)	1.05 (s, 3H)	4.44 (68, d, 1H), 1H[f]	3.56 (s, 3H). 2.60 (s, 3H)	
2m	[PtCl(SnMe_2Cl)(dmphen){*E*-(*i*-Pr)O_2CCH=CHCO_2(*i*-Pr)}]	0.88 (s, 3H), 0.18 (s, 3H)	4.19 (70, ABq, 2H)	3.51 (s, 3H), 3.17 (s, 3H)	5.12 (h, Me_2*CH*O, 1H), 5.04 (h, Me_2*CH*O, 1H)
2n	[PtCl(SnMePhCl)(dmphen){*E*-(*i*-Pr)O_2CCH=CHCO_2(*i*-Pr)}] (isomer, 70% abundance)	1.04 (s, 3H)	4.40 (68, d, 1H), 4.11 (71, d, 1H)	3.57 (s, 3H), 2.56 (s, 3H)	5.15 (h, Me_2*CH*O, 1H), 5.07 (h, Me_2*CH*O, 1H)
2o	[PtCl(SnMe_2Cl)(dmphen){*E*-(*t*-Bu)O_2CCH=CHCO_2(*t*-Bu)}]	0.84 (s, 3H), 0.17 (s, 3H)	4.10 (69, ABq, 2H)	3.50 (s, 3H), 3.20 (s, 3H)	1.57 (s, *t*-BuO, 9H), 1.53 (s, *t*-BuO, 9H)
2p	[PtCl(SnMe_2Cl)(dmphen)(*E*-PhO_2CCH=CHCO_2Ph)][d]	0.92 (s, 3H), 0.19 (s, 3H)	4.55 (71, d, 2H)	3.50 (s, 3H), 3.36 (s, 3H)	
2q	[PtCl(SnMe_2Cl)(dmphen){*E*-(*p*-ClPh)-O_2CCH=CHCO_2(*p*-ClPh)}][d]	0.91 (s, 3H), 0.16 (s, 3H)	4.52 (72, d, 2H)	3.47 (s, 3H), 3.31 (s, 3H)	
2r	[PtCl(SnMe_2Cl)(dmphen){*E*-(*p*-MePh)-O_2CCH=CHCO_2(*p*-MePh)}][d]	0.91 (s, 3H), 0.18 (s, 3H)	4.52 (70, d, 2H)	3.50 (s, 3H), 3.34 (s, 3H)	2.38 (s, Me, 3H), 2.34 (s, Me, 3H)
2s	[PtCl(SnMe_2Cl)(pimpy)(*E*-MeO_2CCH=CHCO_2Me)] (isomer, 75% abundance)	0.88 (s, 3H), 0.09 (s, 3H)	4.20 (71, s, 2H)	3.27 (s, 3H)	9.15 (43, s, N=CH, 1H), 3.76 (s, MeO, 3H), 3.53 (s, MeO, 3H)
2t	[PtCl(SnMe_2Cl)(pimpy)(*E*-EtO_2CCH=CHCO_2Et)] (isomer, 80% abundance)	0.87 (s, 3H), 0.11 (s, 3H)	2H[f]	3.27 (s, 3H)	9.13 (43, s, N=CH, 1H)
2u	[PtCl(SnMe_2Cl)(pimpy){*E*-(*i*-Pr)O_2CCH=CHCO_2(*i*-Pr)}] (isomer, 80% abundance)	0.86 (s, 3H), 0.16 (s, 3H)	4.12 (70, ABq, 2H)	3.28 (s, 3H)	9.12 (45, s, N=CH, 1H), 5.11 (h, Me_2*CH*O, 1H), 4.75 (h, Me_2*CH*O, 1H)
2v	[PtCl(SnMe_2Cl)(pimpy){*E*-(*t*-Bu)O_2CCH=CHCO_2(*t*-Bu)}] (isomer, 85% abundance)	0.82 (s, 3H), 0.21 (s, 3H)	4.05 (70, ABq, 2H)	3.27 (s, 3H)	9.12 (42, s, N=CH, 1H), 1.52(s,*t*-BuO,9H), 1.50 (s, *t*-BuO, 9H)
2x	[PtCl(SnMe_2Cl)(mphen)(*E*-MeO_2CCH=CHCO_2Me)] (isomer, 90% abundance)	0.83 (s, 3H), 0.24 (s, 3H)	4.32 (70, d, 1H), 4.16 (72, d, 1H)	3.20 (s, 3H)	9.85 (48, s, N=CH, 1H), 3.83 (s, MeO, 3H), 3.81 (s, MeO, 3H)
2y	[PtBr(HgMe)(dmphen)(*Z*-MeO_2CCH=CHCO_2Me)][g]	0.70 (s, 3H)	4.11 (81, s, 2H)	3.33 (s, 6H)	3.76 (s, MeO, 6H)
2w	[PtI(HgMe)(dmphen)(*Z*-MeO_2CCH=CHCO_2Me)][g]	0.69 (s, 3H)	4.26 (81, s, 2H)	3.34 (s, 6H)	3.76 (s, MeO, 6H)
2z	[PtCl(HgCF_3)(dmphen)(*Z*-MeO_2CCH=CHCO_2Me)]		4.10 (78, s, 2H)	3.32 (s, 6H)	3.81 (s, MeO, 6H)

[a] The spectra have been recorded at 200, 270, or 400 MHz. $CDCl_3$ has been used as solvent, $CHCl_3$ (δ = 7.26 ppm) as internal standard. Abbreviations: s, singlet; d, doublet; dd, double doublet; t, triplet; q, quartet; h, heptet; m, multiplet. [b] $^2J_{Pt-H}$ in parentheses. [c] $^3J_{Pt-H}$ in parentheses. [d] In $C_2D_2Cl_4$, C_2DHCl_4 (δ = 5.98 ppm) as internal standard. [e] $^2J_{Pt-H}$ not measurable. [f] Overlapped by other signals. [g] Recorded at 248 K.

the stability of the adducts does not appreciably change along the series R = Me, Et, and *i*-Pr.

The trend observed may be substantially related to the higher donor ability of the bulkier alkyls. On the other hand, the influence of steric factors could also be considered. The above results may suggest that increased hindrance of the CO_2R groups more significantly lowers the conformational freedom of these groups around C−C and C−O bonds in the three-coordinate species but has little effect on the corresponding ad-

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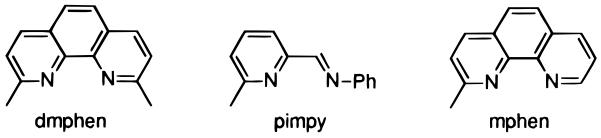

Figure 1. N−N ligands used in this work.

$$[Pt(dmphen)(E\text{-}RO_2CCH{=}CHCO_2R)] + E\text{-}R'O_2CCH{=}CHCO_2R' = [Pt(dmphen)(E\text{-}R'O_2CCH{=}CHCO_2R')] + E\text{-}RO_2CCH{=}CHCO_2R \quad (4)$$

ducts. This may happen because the axial ligands are very effective in restricting the intramolecular mobility, possibly also through the carbonyl−tin interaction (see below), and the additional constraints of bulkier R groups do not increase the molecular rigidity any further. This agrees with the ΔS_{add} values which have been measured for some dmphen and pimpy dialkyl fumarate derivatives (Table 2). As plausible for a process which determines a formal reduction in the number of molecules, the ΔS_{add} values are negative. They increase as the bulkyness of the alkyl group increases, which may reflect a progressively reduced difference between the intramolecular rigidity of the three-coordinate complex and of the corresponding five-coordinate adduct. In agreement, in the case of dmphen, which is more effective than pimpy in reducing the intramolecular mobility of its complexes, the ΔS_{add} values are less negative, and the difference between the homologous Me and Et fumarate derivatives, i.e. **2i** and **2k**, is also smaller than that of the corresponding pimpy derivatives (i.e. **2s** and **2t**).

Instead, if the trend observed stemmed from steric interligand hindrance, it would be due to higher crowding of the olefin and of the chelate around the metal in substrate **1** than in the adduct. The X-ray structures of a type **2** fumarate adduct and of its parent type **1** precursor (see below) show that the Pt−N(chelate) and Pt−C(olefin) are shorter in the trigonal compound; however, the differences are quite small.

As for the interaction of olefin substituents with the axial ligands, it should be noted that already reported structural data concerning type **2** lead[14] and mercury[8] compounds show that carbonyl groups of dimethyl maleate interact with the metal in axial position. These interactions are an additional stabilization factor for type **2** adducts. As reported below, the X-ray structures analysis of $[PtCl(SnMe_2Cl)(dmphen)(E\text{-}MeO_2CCH{=}CHCO_2Me)]$ (**2i**) discloses the interaction of one fumarate carbonyl with the tin atom. The persistence of similar interactions in solution can be reasonably hypothesized. We note that the ^{13}C chemical shifts of the two carbonyl groups in **2i** in $CDCl_3$ are 180.2 and 170.8 ppm, respectively. The difference is very large if compared to that measured for the related mononuclear complex $[PtI(Me)(dmphen)(E\text{-}MeO_2CCH{=}CHCO_2Me)]$, in which no intramolecular interaction is expected. In this case the carbonyl groups resonate at 172.0 and 171.7 ppm, respectively. However, the data available to date are insufficient to be able to assess the diagnostic value of the carbonyl shift concerning intramolecular coordination in **2**.

It should be noted that the factors (i)−(iii) can all be affected by the stereochemistry (i.e. *E* versus *Z*) of a disubstituted olefin ligand. In fact, the *Z* geometry is more favorable to the addition when the olefin is 1,2-dicarboxymethylethene (see Table 2). Since dimethyl maleate is a better donor than dimethyl fumarate,[15] this is in agreement with the above observations on influence (i). On the other hand, in the case where the olefin is maleate, influences (ii) and (iii) depend on the geometrical isomerism of the adduct. Previous results concerning two five-coordinate maleate complexes[8,14] disclosed the carbomethoxy groups pointing toward the bulkier axial ligand, i.e. the organometal fragment. Thus, if the maleate type **2** tin derivatives have the same geometry, it is likely that factor (ii) hinders the addition, while (iii) cooperates with electronic effects in stabilizing the adduct.

Substituents on Tin and Mercury. Taking into account that mercury and tin are reduced upon addition, the high electron-acceptor ability of the groups remaining after the reaction on these atoms should in principle favor the addition. An unfavorable inductive influence on the platinum oxidation of acceptor substituents bonded to the other metal should be of less importance. On the grounds of the stereochemistry of the electrophilic centers, steric hindrance should be much more important in the case of tin than for mercury derivatives.

In fact, in the case of mercury its linear coordination geometry ensures that the electronic effect can be distinguished from steric influence. Adding MeHgCl to $[Pt(dmphen)(Z\text{-}MeO_2CH{=}CHCO_2Me)]$ produces a reversible equilibrium ($pK_{298K} = -1.8$) while the reaction of CF_3HgCl with the same substrate is virtually quantitative. This fact is clearly due to electronic effects and also agrees with the higher Hg−Cl dissociation energy[16] in MeHgCl with respect to CF_3HgCl. As for steric influence, it is found that on changing R from methyl to *tert*-butyl in RHgCl, the stability of the adduct obtained from $[Pt(dmphen)(Z\text{-}MeO_2CH{=}CHCO_2Me)]$ is decreased as expected (see Table 2). Yet, again with regard to the geometry of the Pt−Hg−R sequence, it seems more significant that the slight prevalence of the donor ability of the higher R acts in the same direction.

A clear trend is observed in the addition of halostannanes R_xSnX_y. Equilibrium oxidation constants increase along the series Me_3SnCl, Me_2SnCl_2, and $MeSnCl_3$. More specifically, in the case of $[Pt(dmphen)(E\text{-}MeO_2CH{=}CHCO_2Me)]$ no addition is observed with the monochlorostannane, a reversible equilibrium ensues with the dichloro derivative, and a virtually complete formation of the five-coordinate adduct is detected in the case of the last compound. A substantial influence of the steric factors is unlikely, considering that Me and Cl have similar size. Results concerning the addition of Me_2SnCl_2, $MePhSnCl_2$, and Ph_2SnCl_2 are also in agreement with the prominence of electronic influence. In fact, an increased stability of the addition product from $[Pt(dmphen)(E\text{-}MeO_2CH{=}CHCO_2Me)]$ is observed along the above series, due to the lower donor ability of Ph with respect to Me. It should be remembered that

(14) Albano, V. G.; Castellari, C.; Monari, M.; De Felice, V.; Ferrara, M. L.; Ruffo, F. *Organometallics* **1995**, *14*, 4213−4221.

(15) van Asselt, R.; Elsevier, C. J.; Smeets, W. J. J.; Spek, A. L. *Inorg. Chem.* **1994**, *33*, 1521−1531.

(16) Values of the Hg−halogen dissociation energies (ΔE_{el}) in MeHgX (X = Cl, 88.50; X = Br, 80.47; X = I, 72.05 kcal mol^{-1}) and in CF_3HgCl (75.7 kcal mol^{-1}) were calculated by DFT methods by Prof. V. Barone and are to be published.

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Table 2. Thermodynamic Parameters for Type 3 Reactions

substrate	electrophile	$-pK_{add}$[a]	DH[b]	DS[c]
[Pt(dmphen)(*E*-NCCH=CHCN)]	Me_2SnCl_2	*d*		
[Pt(dmphen)(CH_2=CHCN)]	Me_3SnCl	*d*		
[Pt(dmphen)(*E*-MeO_2CCH=$CHCO_2Me$)]	$(t\text{-Bu})_2SnCl_2$	*d*		
[Pt(dmphen)(*Z*-MeO_2CCH=$CHCO_2Me$)]	*t*-BuHgCl	*d*		
[Pt(dmphen)(CH_2=CHCN)]	Me_3SnBr	1.1		
[Pt(dmphen)(CH_2=CHCN)]	Me_3SnI	3.4		
[Pt(dmphen)(*E*-ClCH=CHCl)]	Me_2SnCl_2	3.3		
[Pt(dmphen)(*E*-PhOCCH=CHCOPh)]	Me_2SnCl_2	3.8		
[Pt(dmphen)(*E*-MeO_2CCH=$CHCO_2Me$)]	Me_2SnCl_2	2.9	-12 ± 1	-26 ± 4
[Pt(dmphen)(*E*-MeO_2CCH=$CHCO_2Me$)]	$MePhSnCl_2$	3.7[e]		
[Pt(dmphen)(*E*-EtO_2CCH=$CHCO_2Et$)]	Me_2SnCl_2	3.2	-11 ± 1	-23 ± 3
[Pt(dmphen)(*E*-EtO_2CCH=$CHCO_2Et$)]	$MePhSnCl_2$	4.0[e]		
[Pt(dmphen){*E*-(*i*-Pr)O_2CCH=$CHCO_2$(*i*-Pr)}]	Me_2SnCl_2	3.8		
[Pt(dmphen){*E*-(*i*-Pr)O_2CCH=$CHCO_2$(*i*-Pr)}]	$MePhSnCl_2$	>4.1[e]		
[Pt(dmphen)(*E*-PhO_2CCH=$CHCO_2Ph$)]	Me_2SnCl_2	1.4[f]		
[Pt(dmphen){*E*-(*p*-ClPh)O_2CCH=$CHCO_2$(*p*-ClPh)}]	Me_2SnCl_2	1.2[f]		
[Pt(dmphen){*E*-(*p*-MePh)O_2CCH=$CHCO_2$(*p*-MePh)}]	Me_2SnCl_2	1.6[f]		
[Pt(pimpy)(*E*-MeO_2CCH=$CHCO_2Me$)]	Me_2SnCl_2	3.4[e]		
		3.3[g]	$-17^g \pm 1$	$-41^g \pm 4$
		2.8[h]	$-14^h \pm 1$	$-34^h \pm 3$
[Pt(pimpy)(*E*-EtO_2CCH=$CHCO_2Et$)]	Me_2SnCl_2	3.7[e]		
		3.6[g]	$-15^g \pm 1$	$-33^g \pm 4$
		3.0[h]	$-13^h \pm 2$	$-30^h \pm 4$
[Pt(pimpy){*E*-(*i*-Pr)O_2CCH=$CHCO_2$(*i*-Pr)}]	Me_2SnCl_2	3.8[e]		
		3.7[g]	$-13^g \pm 1$	$-27^g \pm 2$
		3.1[h]	$-11^h \pm 1$	$-22^h \pm 1$
[Pt(mphen)(*E*-MeO_2CCH=$CHCO_2Me$)]	Me_2SnCl_2	2.8[e]		
[Pt(dmphen)(*Z*-MeO_2CCH=$CHCO_2Me$)]	MeHgCl	1.8		
[Pt(dmphen)(*Z*-MeO_2CCH=$CHCO_2Me$)]	MeHgCl	3.0[i]		
[Pt(dmphen)(*Z*-MeO_2CCH=$CHCO_2Me$)]	MeHgBr	2.9[i]		
[Pt(dmphen)(*Z*-MeO_2CCH=$CHCO_2Me$)]	MeHgI	2.4[i]		
[Pt(dmphen)(CH_2=CHMe)]	Me_3SnCl	*j*		
[Pt(dmphen)(C_2H_4)]	Me_3SnCl	*j*		
[Pt(dmphen)(CH_2=$CHCO_2Me$)]	Me_2SnCl_2	*j*		
[Pt(dmphen)(CH_2=CHCN)]	Me_2SnCl_2	*j*		
[Pt(dmphen)(*Z*-MeO_2CCH=$CHCO_2Me$)]	Me_2SnCl_2	*j*		
[Pt(dmphen)(*E*-MeO_2CH=$CHCO_2Me$)]	Ph_2SnCl_2	*j*		
[Pt(dmphen)(*Z*-MeO_2CCH=$CHCO_2Me$)]	CF_3HgCl	*j*		

[a] At 298 K in $CDCl_3$ (the estimated error is less than ±0.2). [b] In kcal mol^{-1}. [c] In cal mol^{-1} K^{-1}. [d] No appreciable amount of product was observed. [e] Global constant, involving the sum of the concentrations of the two type **2** isomers. [f] At 298 K in $C_2D_2Cl_4$. [g] Referred to the formation of the more abundant isomer. [h] Referred to the formation of the less abundant isomer. [i] At 248 K in $CDCl_3$. [j] Quantitative formation of the product was observed.

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the same trend characterizes the relative stability of the compounds [$PtClMe_2(SnR_nCl_{3-n})$(*N*,*N*′-chelate)] obtained by the oxidative addition of organotin halides to [$PtMe_2$-(*N*,*N*′-chelate)].[7a] These reactions are quite similar to (3) but involve the Pt(II)/Pt(IV) couple.

As for the steric hindrance of the groups bonded to tin, an unfavorable influence on the addition cannot be discarded. We note that no measurable amount of the adduct from (*tert*-butyl)$_2SnCl_2$ and [Pt(dmphen)(*E*-MeO_2-CH=$CHCO_2Me$)] was observed after 14 h in $CDCl_3$, while the rapid addition of Me_2SnCl_2 to the same substrate affords a high yield of the adduct (Table 2).

Axial Halogen Ligand. Given the increase in oxidation number of platinum upon addition, it is expected that a high electron withdrawing ability of the halogen moving onto it from the other metal may hinder the reaction. As a matter of fact, in the equilibrium involving the substrates [$PtMe_2$(*N*,*N*-chelate)] and organotin halides it has been observed that bromide affords a more stable adduct than chloride.[7b] On the other hand, another guideline to the razionalization of the influence of the halogen moving onto the metal is given by its polarizability. The order $K_{eq}(Br) > K_{eq}(Cl)$ for the above mentioned Pt(II)/Pt(IV) equilibrium[7b] also reflects the higher affinity of the softer base Br^- with the acid Pt(IV), which is softer than Sn(IV).

As for the processes described here, comparing equilibria differing only in the halogen which moves onto the axial position appeared to be easy in the case of the addition of an organomercury halide. In fact, in this case the moving halogen is also the only halogen present in the electrophile. We have measured the equilibrium constants for the addition of methylmercury halides MeHgX (X = Cl, Br, I) to [Pt(dmphen)(*Z*-MeO_2CH=C-HCO_2Me)]. The experiments were performed at 248 K in order to slow the chemical exchange, which occurs very rapidly at room temperature.[8a] The corresponding addition pK_{248K} values are respectively −3.0, −2.9, and −2.4. This trend is in agreement with the ΔH_{add} changes[17] involved in the reactions. In fact, [ΔE_{el}(Cl−HgMe) − ΔE_{el}(Pt−Cl)] is close to [ΔE_{el}(Br−HgMe) − ΔE_{el}(Pt−Br)], and these two values are lower than [ΔE_{el}-(I−HgMe) − ΔE_{el}(Pt−I)] of ca. 3 kcal/mol.

Concerning the addition of organotin electrophiles, we note that diorganotin dihalides proved to be the most useful ligands in order to achieve reversible equilibria. However, while mixed-dihalo compounds may in principle be used in order to perform reactions with the sole variation of the moving halogen, possible scrambling of halogen and/or nonchemoselective processes may pre-

(17) Assuming that the difference in the Pt−X bond dissociation energies of different compounds corresponds to the mean values of ref 7b and that thermal and zero point effects are negligible ($\Delta H \approx \Delta E_{el}$), we considered the following: $\Delta H_{add} = \Delta E_{el}(X-MR_mX_{n-1}) - [\Delta E_{el}(Pt-MR_mX_{n-1}) + \Delta E_{el}(Pt-X)]$. The $\Delta E_{el}(Pt-MR_mX_{n-1})$ values were considered to be constant along the series Cl, Br, and I, provided the only variation was the transferred halogen. Thus, the difference in ΔH_{add} between the addition of two homologous organometal halides is as follows: $[\Delta E_{el}(X-MR_mX_{n-1}) - \Delta E_{el}(Pt-X)] - [\Delta E_{el}(X'-MR_mX_{n-1}) - \Delta E_{el}(Pt-X')]$.

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vent a clear-cut analysis of the results. Thus, the use of monohalides was attempted. By reacting Me_3SnX electrophiles (X = Cl, Br, I) with the same Pt(0) complex, i.e. [Pt(dmphen)(CH_2=CHCN)], we were able to assess a stability order, which was reversed with respect to that observed in the addition of organomercury halides. In fact, while Me_3SnCl does not appreciably add to the substrate, a reversible equilibrium operates in the case of Me_3SnBr, and an increased yield of the five-coordinate product forms when Me_3SnI is used. Also in this case, as well as for the Pt(II)/Pt(IV) equilibria mentioned above,[7a] the ΔH_{add} changes agree with the experimental trend as their values decrease according to the following order: $[\Delta E_{el}(I-SnMe_3) - \Delta E_{el}(Pt-I)] < [\Delta E_{el}(Br-SnMe_3) - \Delta E_{el}(Pt-Br)] < [\Delta E_{el}(Cl-SnMe_3) - \Delta E_{el}(Pt-Cl)]$.

It is interesting to note that the difference between the behavior of tin and mercury derivatives is in agreement with the HSAB principle, which indicates the hardness order for the three acid centers: Hg(II) < Pt(II) < Sn(IV). Thus, as the hardness of the halide ion increases (I < Br < Cl), the Sn(II)−X bond becomes more favored with respect to the corresponding Pt(II)−X bond. The halogen effect is reversed for the Pt(II)/Hg(II) couple, due to the fact that Hg(II) can be considered softer than Pt(II).

***N,N*-Chelate.** It was possible to measure the equilibrium constants for the addition of the same electrophile, i.e. Me_2SnCl_2, to two trigonal species bearing the same olefin, i.e. *E*-MeO_2CCH=$CHCO_2Me$, and different chelates, i.e. dmphen and mphen. Very little difference was observed concerning the position of the equilibrium. Thus, it is inferred that increasing the in-plane hindrance of the chelate does not substantially affect the reductive elimination process, whereas, as expected,[6] it hinders the olefin elimination from type **2** species. In fact, the equilibrium in the case *N,N*-chelate = mphen is not limited to the addition/elimination process and the olefin release from the adduct is also observed (eq 5).

$$[Pt(mphen)(E\text{-}MeO_2CH{=}CHCO_2Me)] + Me_2SnCl_2 = [PtCl(SnMe_2Cl)(mphen)(E\text{-}MeO_2CH{=}CHCO_2Me)] = [PtCl(SnMe_2Cl)(mphen)] + E\text{-}MeO_2CH{=}CHCO_2Me \quad (5)$$

As far as we know, this is the very first observation of a multiple equilibrium involving the trigonal species **1**, the TBP adduct **2**, and the related square planar product which has no olefin.

In the case of the less rigid chelate pimpy the addition is more favored with respect to the two phenanthroline derivatives. Thus, electronic effects appear more significant than steric influences, since pimpy presents a steric hindrance comparable to that of dmphen and is more basic than the other two chelates.

Molecular Structure of [PtCl($SnMe_2$Cl)(dmphen)-(*E*-MeO_2CCH=$CHCO_2Me$)] (2i). A drawing of the structure of the title compound is shown in Figure 2, and bond distances and angles of interest are reported in Table 3. The coordination geometry is the expected one; i.e., the anionic ligands Cl and $SnMe_2$Cl define the axial sites of a trigonal bipyramid [Cl−Pt−Sn angle 177.5(2)°], while the phenanthroline and the fumarate double bond occupy the equatorial coordination sites. The phenanthroline plane is not coincident with the coordination plane [Pt,N(1),N(2)], and it is tilted by 13°

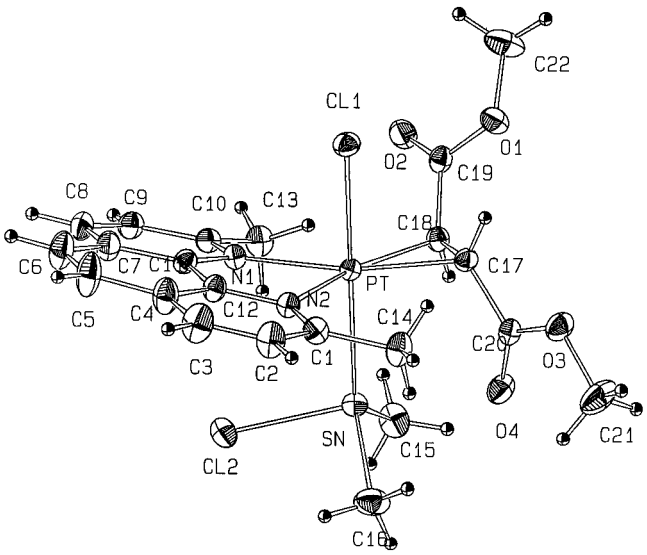

Figure 2. ORTEP drawing of [PtCl($SnMe_2$Cl)(dmphen)-(*E*-MeO_2CCH=$CHCO_2Me$)] (**2i**) with 30% probability displacement ellipsoids for heavy atoms and arbitrarily small radii for hydrogen atoms.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 2i

Pt−C(17)	2.073(6)	C(17)−C(18)	1.454(8)
Pt−C(18)	2.075(6)	C(17)−C(20)	1.498(8)
Pt−N(1)	2.155(5)	C(18)−C(19)	1.492(9)
Pt−N(2)	2.173(5)	C(19)−O(2)	1.196(8)
Pt−Cl(1)	2.476(2)	C(19)−O(1)	1.316(8)
Pt−Sn	2.5864(7)	O(1)−C(22)	1.453(9)
Sn−C(16)	2.142(8)	C(20)−O(4)	1.210(8)
Sn−C(15)	2.134(7)	C(20)−O(3)	1.325(7)
Sn−Cl(2)	2.438(2)	O(3)−C(21)	1.459(9)
Sn−O(4)	2.677(5)		
C(17)−Pt−C(18)	41.0(2)	C(16)−Sn−Pt	119.2(3)
N(1)−Pt−N(2)	76.5(2)	C(15)−Sn−Pt	120.0(2)
Cl(1)−Pt−Sn	177.53(4)	Cl(2)−Sn−Pt	103.62(5)
C(16)−Sn−C(15)	114.4(4)	Cl(2)−Sn−O(4)	174.3(1)
C(16)−Sn−Cl(2)	95.6(3)	C(15)−Sn−C(16)	114.3(4)
C(15)−Sn−Cl(2)	95.8(2)		

toward the chloride ligand in order to optimize the contacts of the methyl groups with the axial ligands. This feature is present in all the compounds of this family. The molecule is chiral because of the prochiral nature of the fumarate ligand and asymmetrical because the conformations of the CO_2Me and $SnMe_2$Cl groups do not conform to any regularity. The conformational asymmetry of the dimethyl fumarate ligand originates from the nonequivalence of the contacts with the axial ligands. In fact, while the CO_2Me group facing the chloride keeps away from this atom, the one facing the $SnMe_2$Cl group is oriented with one oxygen [O(4)] pointing toward the Sn atom. A bonding interaction is established [Sn−O(4) 2.677(5) Å], and the coordination figure at the Sn atom proves to be a distorted trigonal bipyramid. This feature is closely equivalent to that in the lead analogue [PtCl($PbPh_2$Cl)(dmphen)(*Z*-MeO_2CCH=$CHCO_2Me$)][14] in which a similar Pb−O contact [Pb−O = 2.66(1) Å] is present. The Pt−Sn bond [2.586(1) Å] is comparable to that found in [PtCl($SnPh_2$Cl)(dmphen)(C_2H_4)] [2.534(1) Å][5b] and in the above mentioned lead derivative [Pt−Pb = 2.642(1) Å]. The conformation of the $SnMe_2$Cl group around the Sn−Pt axis is controlled by the Sn−O(4) interaction and O(4)−methyl contacts and proves to be skewed with respect to the mirror coordination symmetry around Pt.

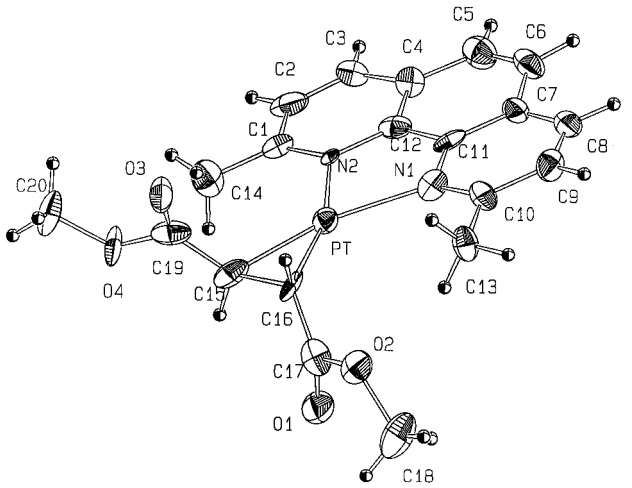

Figure 3. ORTEP drawing of [Pt(dmphen)(*E*-MeO_2-CCH=$CHCO_2Me$)] (**1k**) with 30% probability displacement ellipsoids for heavy atoms and arbitrarily small radii for hydrogen atoms.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 1k

Pt−C(16)	1.88(3)	C(17)−O(1)	1.23(2)
Pt−C(15)	2.09(2)	C(17)−O(2)	1.37(2)
Pt−N(1)	2.12(2)	O(2)−C(18)	1.47(3)
Pt−N(2)	2.07(2)	O(3)−C(19)	1.12(2)
C(15)−C(16)	1.42(3)	O(4)−C(19)	1.40(3)
C(15)−C(19)	1.41(3)	O(4)−C(20)	1.39(2)
C(16)−C(17)	1.42(3)		
C(16)−Pt−C(15)	41.5(7)	N(2)−Pt−N(1)	77.6(6)

The Pt−Cl distance [2.476(2) Å] is equal to that found in the above mentioned tin derivative.[5b] This value is higher than the average value found in the other members of this family of compounds (2.31 Å)[6] and fully confirms that the *trans*-influencing ability of Sn is equivalent to that of the alkyl carbon.

The Pt−C and C=C distances in the fumarate ligand [2.074(6), 1.454(8) Å, respectively] fall in the range of the expected values[6] and, if compared to the corresponding values in [PtCl($SnPh_2Cl$)(dmphen)(C_2H_4)] [2.08(1), 1.41(2) Å], give scant evidence of a stronger platinum to olefin back-donation in the derivative of the more electron-withdrawing fumarate. More indicative of the degree of back-bonding is the substantial bending of the CO_2Me groups away from the Pt atom [C−C=C−C torsion angle 40.41(5)°], even though the optimization of the phenanthroline−fumarate contacts and the Sn···O interaction can play a role.

The dmphen chelate ligand is symmetrically bonded [Pt−N = 2.164(5) Å] and is significantly shorter than in [PtCl($SnPh_2Cl$)(dmphen)(C_2H_4)] [2.20(1) Å].[5b] This difference indicates enhanced nitrogen-to-platinum donation in the presence of a strong platinum-to-olefin back-donation.

Molecular structure of [Pt(dmphen)(*E*-MeO_2C-CH=$CHCO_2Me$)] (1k). The title compound is the three-coordinate precursor of [PtCl($SnMe_2Cl$)(dmphen)-(*E*-MeO_2CCH=$CHCO_2Me$)] described in the preceding section. Its structure is illustrated in Figure 3, and bond parameters of interest are listed in Table 4. The molecule exhibits planar arrangement of the coordinated atoms, as in all the Pt(0) monoolefin complexes. The idealized molecular symmetry is C_2, as imposed by the prochiral nature of the fumarate ligand. The conformations of the CO_2Me appendages approximately conform to this symmetry. Unlike what is found to happen in the five-coordinate species, the phenanthroline plane is almost coincident with the coordination plane defined by Pt, N(1), and N(2) (dihedral angle 2.7°).

The Pt−N and Pt−C interactions exhibit a higher degree of asymmetry than in the five-coordinate companion. The axial ligands in the latter seem to protect the equatorial atoms from strongly asymmetric nonbonded interactions. The Pt−N average distance (2.11 Å) is significantly shorter than the value averaged over all the determinations reported so far for this ligand (2.22 Å).[6] It is also shorter than in the related five-coordinate tin derivative **2i** [2.164(5) Å]. These figures indicate a stronger nitrogen-to-platinum donation in the $16e^-$ Pt(0) molecule.

The Pt−olefin interaction is markedly asymmetric [1.93, 2.07(2) Å], but the average value (2.00 Å) is shorter than the corresponding value in **2i** [2.074(6) Å]. The C=C distance [1.42(2) Å] is in the range of those found for similar compounds.[18] The bending back of the carbon chain [C−C=C-C torsion angle 50(2)°], which is higher than in the five-coordinate species [40.4(5)°], provides more information. This feature is in accordance with a consistent platinum-to-olefin back-donation as a consequence of the above mentioned higher donation from the dinitrogen ligand and higher charge accumulation on the zerovalent metal. The contacts among methyl hydrogens on the phenanthroline ligand and fumarate appendages do not reveal significant features, due to the conformational adaptability of the fumarate ligand.

Conclusion

It has been found that the reactions between organo−tin or −mercury halides with Pt(0) complexes can involve "reversible" equilibria, which can be tuned by the features of each ligand. Thus, this offers rare opportunity to investigate the influence of the different electronic and steric effects in the same system. In all cases the influence observed cannot be confused with a parallel kinetic behavior. It has also been found that the electronic and steric effects can be satisfactorily separated. More particularly, it can be clearly seen that the electron-donor ability of the olefins linked to the metal to be oxidated favors the addition. The reverse holds true for groups on the reduced metal. Furthermore, the guideline offered by the HSAB principle for the rationalization of the equilibrium trends was once again proven to be effective. This explains the observed inversion of the "halogen effect" concerning the adduct stabilization by the halogen moving onto platinum, considering the hardness of the electrophilic metal center. It should also be noted that the thermodynamic trends for the Pt(0)/Pt(II) couples linked by eq 3 conform to those concerning analogous Pt(II)/Pt(IV) equilibria.

Experimental Section

General Comments. NMR spectra were recorded at 400, 270, or 200 MHz on a Bruker AM-400, a Bruker AC-270, or a Varian XL-200 spectrometer, respectively. ^1H NMR data for the new compounds of type **1** and **2** are reported in Table 1.[19] Elemental analyses for representative type **2** complexes are reported in Supporting Information. Complexes **1a**−**j** were

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obtained in high yields as described for [Pt(*N*,*N*′-chelate)($MeO_2CCH{=}CHCO_2Me$)] complexes.[20] Previously described type **1**[20] and **2**[5,8] complexes and the compounds $MePhSnCl_2$,[21] (*tert*-butyl)$_2SnCl_2$,[22] pimpy,[23] mphen,[24] *E*-(*p*-RPh)$O_2CCH{=}CHCO_2$(*p*-RPh) (R = Me, H, Cl),[25] *E*-(*t*-Bu)$O_2CCH{=}CHCO_2$(*t*-Bu),[26] and CF_3HgCl[27] were synthesized according to literature methods. *E*-(*i*-Pr)$O_2CCH{=}CHCO_2$(*i*-Pr) was synthesized by adapting the known procedure for *E*-$EtO_2CCH{=}CHCO_2Et$.[28] The reactions were carried out in air. All the other chemicals were commercially available.

Synthesis of 2a−x. A solution of the organotin halide R_nSnX_m (0.24 mmol) in 1 mL of chloroform was added with stirring to a solution of the appropriate type **1** precursor (0.20 mmol) dissolved in the minimum amount of chloroform. The white to yellow product was crystallized by careful addition of diethyl ether, filtered off, washed with diethyl ether, and dried under vacuum. A second crop of crystals could be obtained by adding more diethyl ether to the mother liquor (yield: >65%). Complexes **2b**,**p**−**r**, highly dissociated in solution, were not isolated in the solid state but only detected in solution through NMR spectroscopy (see below).

Synthesis of 2y−z. The complexes have been obtained by adapting the procedure for [PtCl(HgMe)(dmphen)(*Z*-$MeO_2CCH{=}CHCO_2Me$)].[8a] The appropriate organomercury halide (0.24 mmol) was added to [Pt(dmphen)(*Z*-$MeO_2CCH{=}CHCO_2Me$)] (0.11 g, 0.20 mmol) dissolved in 1.5 mL of chloroform. Slow addition of *n*-hexane afforded pale yellow crystals of the product, which was filtered off, washed with *n*-hexane, and dried under vacuum (yield: >85%).

Determination of the Equilibrium Constants. In a typical experiment 0.005−0.015 mmol of the appropriate type **2** complex was dissolved in 0.800 mL of $CDCl_3$ and the resulting equilibrium mixture monitored through ^1H NMR spectroscopy. In the case of the addition of Me_2SnCl_2 to **1d**−**f** which affords **2p**−**r**, to a solution of the appropriate precursor (0.020 mmol) in 0.700 mL of $C_2D_2Cl_4$ (chosen as solvent in order to improve the solubility of the three-coordinate species) was added 0.0200 mmol of Me_2SnCl_2 in 0.100 mL of $C_2D_2Cl_4$, and the resulting equilibrium mixture monitored through ^1H NMR spectroscopy. The equilibrium constant relative to the addition of Me_3SnBr to [Pt(dmphen)($CH_2{=}CHCN$)] affording **2b** was determined in a similar way, except $CDCl_3$ was used as solvent. The relative concentrations of the reacting species were evaluated by integrating suitable peaks. When more than one type **2** isomer was present in solution, the concentration of the species was expressed as the sum of the isomer concentrations. At least two measurements at different concentrations were performed for each determination. The p*K* values reported in Table 2 are the average of the values calculated from each measurement. The estimated average error is less than 0.2 logarithmic unit. The ΔH and ΔS values reported in Table 2 were obtained through experiments performed at various temperatures in a range typically around 278−323 K. A linear plot of ln K_{add} vs $1/T$ was calculated by using the least-square method on the set of experimental points.

Table 5. Crystallographic Data for Complexes 1k and 2i

	compd	
	1k	**2i**
formula	$C_{20}H_{20}N_2O_4Pt$	$C_{22}H_{26}Cl_2N_2O_4PtSn$
fw	547.47	767.13
cryst syst	monoclinic	triclinic
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
a (Å)	8.081(2)	9.942(2)
b (Å)	17.282(2)	10.872(3)
c (Å)	13.201(2)	13.603(3)
α (deg)	90	79.00(2)
β (deg)	91.04(1)	76.41(2)
γ (deg)	90	63.67(2)
V (Å^3)	1843.4(6)	1274.6(5)
T (K)	293	293
Z	4	2
ρ_{calc} (Mg/m^3)	1.973	1.999
λ(Mo Ka) (Å)	0.710 69	0.710 69
μ(Mo Kα) (mm^{-1})	7.641	6.701
F(000)	1056	732
cryst dimens (mm)	0.08 × 0.10 × 0.15	0.2 × 0.25 × 0.3
transm	0.856−1.000[a]	0.937−1.000[a]
2θ range (deg)	5−54	4−60
R_1[b]	0.0528	0.0424
wR_2[c]	0.1142	0.1096
GooF	0.861	1.038

[a] The data were corrected for the anisotropic absorption by the empirical method (ψ scans). [b] $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$. [c] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Crystallography. The X-ray diffraction experiments were carried out at room temperature on an Enraf-Nonius CAD-4 diffractometer, using Mo Kα radiation. Crystal data and some experimental details of the data collection are reported in Table 5. The crystals of both species did not suffer significant decay. Crystals of **2i** suitable for X-ray experiments were grown by slow diffusion of toluene into a dichloromethane solution. Crystals of **1k** were obtained from chloroform/acetone. Unfortunately, several attempts to grow crystals of **1k** to the desired size were unsuccessful. The measurements of the diffraction intensities for **1k** were carried out on a small crystal, and as a consequence, the structure model is affected by higher errors than **2i**. The structures were solved by Fourier methods (SHELX-86)[29] and refined by full-matrix least-squares calculations (SHELX-93).[29] The structure model comprised anisotropic thermal parameters for the non-hydrogen atoms and idealized positions of the hydrogen atoms.

Acknowledgment. We thank the Consiglio Nazionale delle Ricerche and Ministero dell'Università e della Ricerca Scientifica for financial support and the Centro Interdipartimentale di Metodologie Chimico-Fisiche, Università di Napoli "Federico II", for NMR facilities. We also thank Prof. B. Åkermark and Prof. P. Corradini for helpful discussion.

Supporting Information Available: Tables of fractional coordinates and displacement parameters, selected intramolecular distances and angles, full details of the data collection, hydrogen atom coordinates, and anisotropic thermal parameters for complexes [Pt(dmphen)(dimethylfumarate)] (**1k**) (Tables S1−S5) and [PtCl($SnMe_2Cl$)(dmphen)(dimethylfumarate)] (**2i**) (Tables S6−S10) and a table of elemental analyses for representative new type **2** complexes (Table S11) (14 pages). Ordering information is given on any current masthead page.

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(19) ^1H NMR data for [PtCl($SnMe_2Cl$)(mphen)] [298 K, 200 MHz, in $CDCl_3$, $CHCl_3$ (δ = 7.26 ppm) as internal standard] [abbreviations: s, singlet; d, doublet; q, quartet; dd, double doublet]: 10.63 ($^2J_{Pt-H}$ = 70Hz, N=CH, 1H), 8.55 (d, 1H), 8.43 (d,1H), 8.01 (ABq, 2H), 7.80 (d, 1H), 7.65 (dd,1H), 3.32 (s, NCMe, 3H), 0.88 (s, $SnMe_2Cl$, 6H) ppm.

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