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Hemilability and regioselectivity in palladium and platinum complexes of dppm(*E*) [*E* = O, S, Se] ligands

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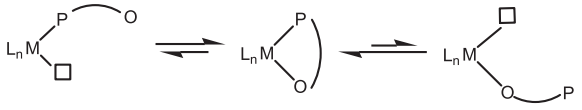
ABSTRACT

Hemilability and nonrigidity in a series of mixed *P^P=E* donor ligands where *E* = O, S, or Se have been studied in palladium and platinum complexes of the type [M{κ^2-(dimethylamino)ethylnaphthyl-*C,N*)}(*P^P=E*)][SbF_6] where *P^P=E* = $Ph_2PCH_2P(E)Ph_2$.The role of the donor in hemilability, regioselectivity and the binding preferences of particular donors *trans* to the metallated carbon atom were also investigated. NMR parameters including couplings to ^{195}Pt and ^{77}Se were investigated for *cis* and *trans* isomers. The magnitude of ^2J $^{13}C-^{77}Se$ couplings can readily distinguish the *cis* and *trans* isomers. A large through-space $^{13}C-^{77}Se$ ^3J coupling was observed in one of the amino methyl groups of the dppm(Se) complexes.

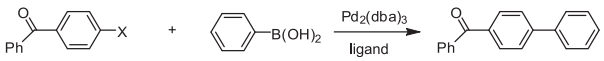
1. Introduction

Hemilabile ligands have played a key role in a number of important reactions catalyzed by transition-metal complexes [1–4]. As an example, a ligand combining two different donors, for example a hard and a soft donor atom combination such as *P^O* can exist in $\kappa^2 \leftrightarrows \kappa^1$ equilibria as shown in Eq. (1), in which the relative concentrations of *O*-bound and *P*-bound complexes depend upon the relative labilities of the M–P and M–O bonds. The opening of the chelate can occur by a dissociative process or be initiated by attack at the metal by solvent or other ligands. The differential donor properties in heterobidentate ligands have been useful in controlling catalytic activity, even in cases where hemilability is not involved. One of the early notable successes associated with complexes of *P^O*-ligands was their application in the Shell higher olefin process which utilizes a nickel-catalyzed oligomerization of ethylene [5].



(1)

Another area of significant activity is in the potential application in C–C bond forming reactions, particularly in the catalysis of Suzuki–Miyaura cross-coupling of haloarenes with arylboronic acids (Eq. (2)) where there has been intense activity recently in an effort to identify systems that can use less reactive haloarenes [6,7].



(2)

Bulky monohapto phosphine ligands can promote the generation of unsaturated palladium(0) and palladium(II) intermediates and enhance their catalytic activity in coupling reactions [8]. Generally, 14-electron intermediates are implicated in many of these reactions, but isolations of such complexes are very rare. The first example of an isolated monomeric (aryl)palladium(II) monophosphine complex was only reported recently by Hartwig [9,10]. Since these intermediates are rare and usually unstable, the potential to stabilize them temporarily with hemilabile ligands is an attractive alternative. During a catalytic cycle, dissociation of the more labile donor can create an open site on the metal for substrate binding, while recoordination of that donor can temporarily stabilize a potentially coordinatively unsaturated metal center that may be generated in another step in the catalytic process. Some of the early bulky ligands which were successful contained an alkoxy group that may have

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acted as a weak or transient donor [11,12]. More recent studies of ligand structure by Buchwald generalized the effectiveness of bulky ligands such as dicyclohexyl(2′,6′-dimethoxybiphenyl)phosphine and the importance of coordinative unsaturation in the mechanism [13]. Increasingly, evidence suggests that hemilability may play a role with these bulky ligands, but that the bonding involves *P^C* chelates rather than *P^O* chelates. We have found that even Cy_2P systems containing a potential chelate with a Me_2N donor linked through a biphenyl backbone actually involve chelation of a *P* and two of the carbons in the biphenyl [14]. There have also been several recent publications suggesting the use of hemilabile ligands for Suzuki couplings [15,16].

Despite recent reviews on the subject [3,4], there is relatively little information on the kinetics in hemilabile systems or the ease of dissociation of one donor of a hemilabile ligand in a given system. Usually, an assertion is made that the system contains a hemilabile ligand, but this has seldom translated into any measurements of the importance of hemilability in a reaction. Even the degree of dissociation of the more labile donor or the rate of its dissociation may be open to wildly different opinions. For example, the monosulfide of BINAP, BINAP(S), was claimed to be a readily-prepared chiral monodentate phosphine in a paper entitled "Diphosphine mono-sulfides: readily available chiral mono-phosphines" [17]. The assumption was made that the P═S would be such a poor donor that the κ^2-*P,S* form would be unstable relative to the κ^1-*P* form. In some cases that may be the true; we, however, have found that the half-life for the interconversion of isomers in a BINAP(S) ruthenium complex [18], which requires a change from κ^2-*P,S* to the κ^1-*P* form, was 22 days, implying that the rate of formation of the κ^1-*P* form was extremely slow and that no significant amount of the κ^1-*P* form would be observable.

We have now investigated complexes of several potentially hemilabile ligands in an effort to assess the importance of the relative hardness of the donors and the relative ease of forming the κ^1-*P* form. In this context we have chosen a series of *P^P═E* (*E* = O, S, Se) chelates bound to a (*C,N*)-cyclometallated (dimethylamino)ethyl-napthylene, [(κ^2-dman-*C,N*)Pd(*P^P═*E)]SbF_6 **1** or [(κ^2-dman-*C,N*)Pt(*P^P═E*)]SbF_6 **2**. This cyclometallated ligand scaffold provides a rigid unsymmetrical framework that avoids complications from conformational equilibria within its five-membered ring, as well as providing donors of significantly different *trans* influence.

2. Results and discussion

2.1. (κ^2-dman-C,N)Pd(dppmE)

It has been suggested, based on the results of a number of X-ray structure determinations of the preferred geometric isomer, that with a heterobidentate chelate bound to (κ^2-dman-*C,N*)Pd, "the softest of the two donors invariably takes up the position *trans* to the Me_2N group" [19–21]. Thus with a *P,O* donor set, the *O* would occupy the site *trans* to the carbon, as in *trans*-**1**. This was, in fact, observed for the relevant case of the binding of the *P^O* donor BINAP(O) [22]. It was of interest to determine if the *cis* isomer would be observed with softer P═E donors. In any case, the relative hemilability of the donors *trans* to the carbon would be relevant in consideration of mechanisms of the Suzuki–Miyaura reactions in the presence of heterobidentate ligands.

The determination of regiochemistry will be discussed relative to the complex **1** containing ligand **a**, shown in Fig. 1. Rather than a bridged dimer, one would anticipate a chelated structure for complexes of **a** as shown for **1a** (*E*═Se) and found in the crystal structure of (dppmSe)Pd(SeCN)(CN) [23]. The downfield shift of the P(III) resonance upon coordination of 64.12 ppm is also indicative of chelation to form a five-membered ring [23]. Expectations are that

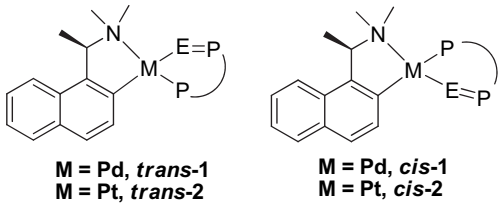


Fig. 1. The isomers of (κ^2-dman-*C,N*)Pd(dppmE) complexes.

the coupling of ^{77}Se with ^{31}P generally would be reduced on binding to the metal with respect to the free phosphine selenide[24] and this change in coupling provides spectroscopic evidence of coordination of the selenium. The $^1J_{Se,P}$ coupling in **a** is 732.3 Hz which is reduced to 571.5 Hz in **1a** Only the *trans* isomer appears to be present as suggested by long range coupling of phosphorus to the carbon and hydrogen nuclei in the methyl groups on the nitrogen as $^3J_{P,C} = 2.5$, ~0.8 Hz and $^4J_{P,H} = 3.4, 1.6$ Hz. Evidence for the *trans* arrangement is also indicated by the absence of a large phosphorus coupling to any of the low field carbon nuclei. In the diphos complex analogous to **1a**, the *ipso* carbon resonates at δ 157.7 and shows $^2J_{P,C}$ of 114.0 and 2.1 Hz for the *trans* and *cis* couplings to the phosphorus. The *E* in a P═E generally does not allow substantial correlations of spin through it such that very small couplings through the chalcogen to the *ipso* carbon would be expected. An appreciation of the attenuation of ^3J couplings to be expected through Se bonds can be found from the example of $N(Ph_2P{=}Se)_2Pd(PMe_2Ph)Cl$ which showed $^3J_{P,P}$ of 16.1 and 12.1 Hz [25].

The ^{77}Se ^2J coupling is also attenuated rapidly since a negligible coupling is observed to the methylene carbon in the ligand in **1a**. The largest $^{77}Se-^{13}C$ coupling observed is the ^2J coupling through palladium to the carbon at δ 153.3 of 30.7 Hz. Hence, it is clear that the observed isomer is that with the P═Se *trans* to C. This is further evidenced by consideration of analogous platinum complexes (*vide infra*). *Thus, even though one might argue that the selenium of the phosphine selenide is the softer donor relative to phosphorus, it occupies the position previously ascribed to the harder donor.* One might also note that an example of a complex with an S-donor *trans* to C was also found for a polycyclic P^P═S variant of **1**. [19] Thus, as observed in earlier arguments regarding hard-soft effects, sometimes the opposite donor is preferred and the selectivity is anti-symbiotic. *This suggests that some revision of the "rule of thumb for isomeric preferences" is in order.*

2.2. (κ^2-dman-C,N)Pt(dppmE)

The assignment of the isomeric structures in the platinum complexes is much more straightforward. The $^{31}P-^{195}Pt$ coupling is strongly influenced by the ligands *trans* to the phosphorus [26], such that typically in complexes of this **L**-*C,N* type with bisphosphine chelates the $^1J_{P,Pt}$ *trans* to carbon is approximately half the magnitude of that *trans* to nitrogen [27]. Upon addition of ligands **a, b,** or **c** to [(κ^2-dman-*C,N*)$PtCl]_2$ both *cis* and *trans* isomers are formed initially in approximately equal amounts and, depending upon conditions, the mixture slowly converts to a single isomer in solution (Fig. 2). Complex **2a** interconverts with a half-life of

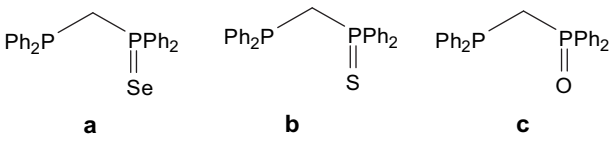


Fig. 2. Heterobidentate ligands investigated.

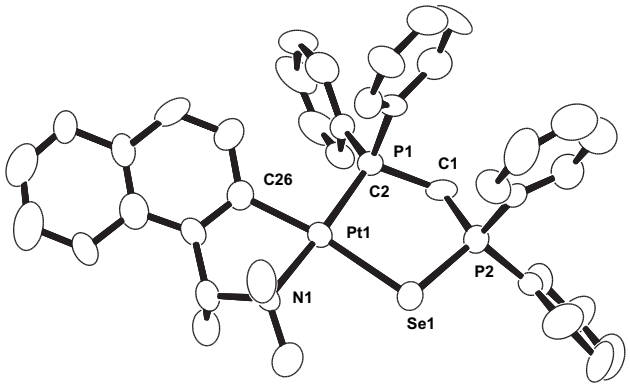


Fig. 3. An ORTEP view of the cation of **2a** showing 50% thermal ellipsoids.

approximately 70 h. Initially, two P(III) resonance patterns are observed for **2a** with 4015 Hz and 2014 Hz $^{1}J_{P,Pt}$ couplings and eventually only the resonances of the isomer with the $^{1}J_{P,Pt} = 4015$ Hz persist. This isomer was purified by recrystallization and identified as the *trans* isomer by an X-ray crystallographic determination (see Fig. 3). An interesting feature of the ^{31}P NMR of the disfavored *cis* isomer is that the ^{31}P signal of the P(V) which is *trans* to N also shows a fairly large coupling to ^{195}Pt of 136 Hz, whereas this coupling is only ~10 Hz when it is *trans* to C. One might anticipate that the ^{13}C spectra would be indicative of the binding modes, but the platinum satellites are broad, such that sensitivity is an issue in locating them. With the ligand enriched in ^{77}Se, ^{77}Se–^{13}C couplings can be readily observed. The ^{77}Se–^{13}C couplings are somewhat smaller than might be expected and attenuate rapidly. A $^{2}J_{Se,C}$ of only 5.0 Hz is resolved in the methylene carbon of *trans*-**2a,** and only one of the aromatic carbons shows a moderately large coupling [δ 142.7, $J_{Se,C}$ = 28.0 Hz $J_{P,C}$ = 5.1, 2.5 Hz], presumably the naphthyl carbon directly bound to platinum. Notably, one of the N-methyl groups in *trans*-**2a** shows a relatively large ^{77}Se–^{13}C coupling (22.8 Hz). As this would correspond to a ^{3}J coupling, it would be expected to have attenuated significantly; hence, it may be enhanced by a through-space mechanism (the closest Se…. C–N distance is 3.212(9) Å). A "^{4}J" ^{77}Se–^{1}H coupling of 7.3 Hz coupling to the N-methyl is also observed in *trans*-**2a**. Comparable values are also observed in *trans*-**1a** for ^{77}Se–^{13}C coupling (21.9 Hz) and ^{77}Se–^{1}H coupling (7.3 Hz). We attribute these unusually large coupling values primarily to through-space coupling, but alternatively, one might invoke a weak bonding interaction between the methyl hydrogen atoms and the selenium [*note that the hydrogen atom positions shown in Fig. 3 are in calculated positions*]. Some contribution to this ^{3}J ^{77}Se–^{13}C coupling could arise from the orientation of the methyl in a *cisoid* arrangement and the involvement of a Karplus-type mechanism; however, an even larger coupling would be expected for one of the *ipso* carbons in the phenyl in a *transoid* position if this were a major factor and this is not observed. In *cis*-**2a** the most downfield resonance in the ^{13}C spectrum, [δ 150.38 (dd, $J_{C,P}$ = 111.9, 10.2 Hz)] has a long relaxation time and also shows a large coupling to ^{31}P as expected for a carbon trans to P.

Table 1
Selected bond lengths (Å) and angles (deg) for **2a** and **2c**.

	2a (E=Se)	2c (E=O)
Pt–P1	2.223 (2)	2.216 (1)
Pt–E	2.500 (1)	2.157 (4)
Pt–N1	2.133 (6)	2.111 (4)
Pt–C26	2.048 (7)	1.977 (5)
P2–E	2.152 (2)	1.522 (4)
Pt–E–P2	101.41 (6)	119.8 (2)
Pt–P1–C1	111.3 (3)	102.7 (2)
E–Pt–P1	91.95 (5)	87.1 (1)
P1–C1–P2	111.2 (4)	107.4 (3)

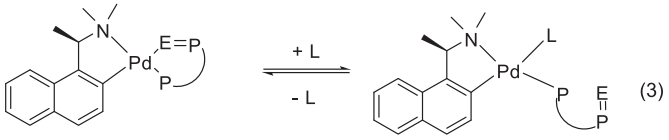
Table 2
Deviation (Å) from the Pt1–N1–C26 plane.

	2a(E=Se)	2c(E=O)
E	0.0523 (10)	−0.0954 (37)
P1	0.0679 (19)	0.0775 (14)
P2	0.1773 (22)	0.0376 (15)

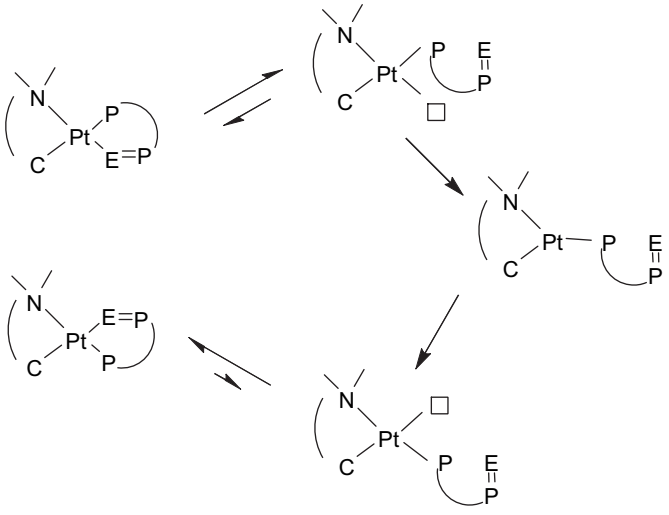
The crystal structures of **2a** and **2c** are similar and some selected bond lengths and angles are given in Table 1. The preference for selenium to bind with angles [M–E–P] closer to 90° and that of oxygen to accommodate a wide range of angles are evident in the relative [Pt–E–P] angles of 101.14(9) and 120.1(3)° respectively. In comparing **a** with **c**, the Pt–P1–C1 bond angle opens significantly in order to accommodate the angle preference, as well as the longer P=E bond length with selenium. A more puckered chelate ring is produced with the selenium ligand as indicated in the deviation of P2 out of the plane containing the platinum, nitrogen and carbon (Table 2).

3. Relative hemilability

None of these palladium and platinum complexes showed any indication of hemilability *via* a dynamic NMR spectrum in the absence of additional ligands. In order to test the relative bond strengths, the palladium complexes were treated with 3,5-lutidine or triphenylphosphine to determine if added ligand could compete with the P=E donor for an open site.



On addition of lutidine, only the ligand with an oxygen donor showed a significant conversion to monodentate coordination. Palladium complex **1c** comprising a dppm(O) ligand showed a mixture of κ^2-*P,O* and κ^1-*P* forms in the presence of added



Scheme 1. Isomerization of a T-shaped intermediate.

Table 3
Comparison of ^{31}P NMR parameters.

	$Ph_2PCH_2P(Se)Ph_2$ ($J_{P,P}$) ($J_{Pt,P}$}	$Ph_2PCH_2P(S)Ph_2$ ($J_{P,P}$) {$J_{Pt,P}$}	$Ph_2PCH_2P(O)Ph_2$ ($J_{P,P}$) {$J_{Pt,P}$}
Free ligand	−27.48 [^3J = 14.1]; 30.75 (85.3) [^1J = 732.0]	−28.44; 39.96 (77.2)	−28.62; 27.76 (50.1)
Pd κ^2	36.44[5.7]; 30.47 (34.0) [571.5]	34.22; 47.20 (30.3)	27.93; 52.80 (17.8)
Pd κ^1	–	–	24.34; 31.11 (br)
Pt κ^2	*cis* 28.36 [4.1]{2013.5}; 36.10 (68.0)[521]{136.4} *trans* 17.02 [5.4]{4014.8}; 30.42 (25.9)[549]{10}	*cis* 24.93 {1965.2}; 56.55 (63.1){135} *trans* 14.84 {4000.2}; 49.02 (23.0){11}	*cis* 22.09 {1900.5}; 73.22 (33.2){∼120 br} *trans* 11.23 {4064.7}; 60.25 (10.8)]{∼10 br}
Pt κ^1	–	–	7.42 {4072.0}; 25.22 (br)

3,5-lutidine. The ^{31}P NMR showed two pairs of doublets at low temperature and broadening at room temperature attributable to more rapid interconversion of κ^2-*P,O* and κ^1-*P* complexes as shown in Eq. (3). The extent to which the κ^1-*P* complex was formed depended upon the relative amount of lutidine added, the displacement of the P═O donor by the lutidine being essentially quantitative. Similar behavior was found for **1c** and **2c**, where the P═O was again selectively displaced by the lutidine. In the case of *trans*-**2c**, two different sets of P(III) resonances were observed in the ^{31}P NMR spectrum at room temperature after addition of lutidine with two different, but large, values for $^{195}Pt-^{31}P$ coupling (κ^2 4145 Hz; κ^1 4072 Hz) supporting the assignment as κ^1-*P* rather than κ^1-*O*. In both complexes the large $^1J(^{195}Pt,^{31}P)$ indicates that the P(III) is *trans* to the Me_2N. The upfield shift of the P(III) resonance also suggests the loss of the chelate ring in forming the κ^1-complex [28]. The spectra broaden above room temperature indicative of interconversion of the κ^2-*P,O* and κ^1-*P* complexes.

None of the complexes comprising bisphosphine monosulfide or -monoselenide ligands showed any indication of displacement of either donor by NMR in the presence of added lutidine. This would seem to indicate that the P═S and P═Se donors form less labile interactions with the palladium and platinum centers than the P═O, an observation consistent with HSAB ideas. It also true, however, that the chelate rings formed exhibit different bond angles and ring geometries which may also contribute significantly to the differences in lability.

When triphenylphosphine was added to solutions of the complexes **1a**–**c** or **2a**–**c**, neither coordination of the added phosphine nor the formation of κ^1-*P* species was observed. Addition of triphenylphosphine selenide to a solution of the palladium precursor [(κ^2-dman-*C,N*)PdCl]$_2$ gives rise to a rapid exchange of the two halves of the dimer that is evidenced by the conversion of the two signals due to the unique methyl protons seen in the ^1H NMR of the precursor to a single doublet. This indicates a reversible bridge-cleaving and complexation of the phosphine selenide. This reversible coordination shows that a monodentate phosphine selenide is not a strong ligand for the [(κ^2-dman-*C,N*)PdCl] fragment in the absence of a second donor to give a chelate, an observation suggesting that, in designing hemilabile ligands, it is critical to consider the ligand as a whole rather than taking the different donors in isolation.

A simple mechanism for the *cis*–*trans* isomerization would involve the formation of the κ^1 intermediate and its interconversion *via* a T–Y–T rearrangement as shown in Scheme 1. The relatively slow *cis* to *trans* isomerizations of the sulfide and selenium complexes in the platinum complexes [$t_{1/2}$ (**2a**) ∼ 70 h; $t_{1/2}$ (**2b**) ∼ 140; $t_{1/2}$ (**2c**) ∼ 20 h] further suggest that the hemilability in these complexes is limited, but with **2c** the fastest. The T–Y–T interconversion would be expected to have a lower barrier [29–32], especially since the P(III) is *trans* to the labilizing carbon. These slow rates of isomerization presumably reflect the greater difficulty of breaking the Pd–S and Pd–Se bonds.

Table 4
Selenium-77 NMR parameters.

	δ	$^1J(^{31}P-^{77}Se)$	$^3J(^{31}P-^{77}Se)$	$^1J(^{195}Pt-^{77}Se)$
Free dppmSe	−292.5	732	13.1	
Pd (**1a**)	−116.0	572	No	
Pt (**2a**) *trans*	−107.0	549	No	363
Pt (**2a**) *cis*	−51.0	521	No	265

4. NMR assignments

Since ^{31}P resonances for phosphines generally shift downfield considerably upon coordination, these resonances are generally in the same region of the spectrum as those for the P(V) resonance of the P═E. It is generally difficult to conclusively assign these resonances in bisphosphine monoxide and monosulfide palladium complexes. For the monoselenides, the ^{77}Se satellites reliably indicate the P(V) resonance. Fortunately, the ^{195}Pt satellites conclusively identify the P(III) resonances in the platinum complexes. The ^{31}P data for the complexes studied are summarized in Table 3.The coordination shifts for the P(III) in *cis*-**2a** and *trans*-**2a** are 55.84 ppm and 44.50 ppm, respectively. The shifts are large

Table 5
Crystallographic data.

	2a	**2c**
Color, shape	Pale yellow, block	Colorless, block
Empirical formula	$C_{40}H_{40}Cl_2F_6NP_2PtSbSe$	$C_{79}H_{78}Cl_2F_{12}N_2O_2P_4Pt_2Sb_2Se_2$
Formula weight	1177.41	2143.96
Radiation/Å	Mo-Kα (monochr.) 0.71075	Mo-Kα (monochr.) 0.71075
T/K	223	223
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$ (No. 19)	$P2_12_12_1$ (No. 19)
Unit cell dimensions		
a/Å	12.7033 (5)	12.8402 (4)
b/Å	17.3755 (7)	18.4915 (5)
c/Å	19.8277 (8)	18.3289 (5)
V/Å^3	4376.5 (3)	4351.9 (2)
Z	4	2
D_{calc}/g cm^{-3}	1.787	1.636
μ/cm^{-1} (Mo-Kα)	48.778	40.080
Crystal size/mm	0.20 × 0.10 × 0.10	0.19 × 0.15 × 0.15
Refl: total, unique, Frpairs	45234, 9880, 4430	45701, 9904, 4428
R_{int}	0.0722	0.0484
No. Obs	9880	9904
Parameters	487	523
$R_1^{a)}$, $wR_2^{b)}$, GOF	0.0473, 0.1018, 1.046	0.0362, 0.0737, 1.071
$R_1^{a)}$, $wR_2^{b)}$, GOF inverted	0.0732, 0.1782, 1.773	0.0691, 0.1675, 2.365
Flack parameter	0.036 (7)	0.004 (5)
Resid. density/*e* Å^{-3}	−1.12 < 2.25	−0.42 < 0.93

a) $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, for all $I > 2\sigma(I)$; b) $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

owing to the inclusion in a chelate ring [28] and the difference presumably largely reflects the difference in *trans* influence of the N and C. On the other hand, the coordination shifts for the P(V) associated with Se binding in *cis*-**2a** and *trans*-**2a** are 5.35 ppm and −0.33 ppm, respectively. The P(V) coordination shifts observed in **2b** and **2c**, however, are substantial (34.54 ppm for *trans*-**2c**). A markedly larger coordination shift was observed for P(III) in *trans*-**1a**, consistent with typical behavior seen for second versus third row transition metals; however only a minor shift was observed for P(V). In the case of **1a** and **2a** the changes in δ of the P(V) resonances are distinctly smaller than observed in **b** and **c** analogs, perhaps due to the difference in the geometries of the selenium-containing rings with respect to those containing oxygen or sulfur. The large variability of the shifts upon coordination suggests that assignments to P(III) and P(V) in palladium complexes of ligands similar to **b** and **c** should be made with caution.

The $^2J_{P,P}$ coupling generally decreases upon binding of the free ligand in a chelate. This coupling is also much larger (~3 times as much) in the *cis* complexes than in the *trans* complexes. The ^{77}Se data (Table 4) show downfield coordination shifts upon binding in a chelate. The coordination shifts are larger for the palladium complex than for the platinum complexes, which is in opposition to the trend observed for P(III) binding.

5. Conclusion

Within the series of palladium and platinum complexes of bisphosphine monochalcogens studied, it seems that only the bisphosphine monoxides show any propensity for hemilabile behavior in the presence of strong nucleophiles. This is probably largely a result of the preference of the soft metals used for the softer donors sulfur and selenium, with which they form stronger interactions. The extent to which differences in the conformation of the metallo-bisphosphine monochalcogen rings also influence this behavior is not clear but from the crystallographic studies it can be seen that these differences are significant.

6. Experimental

All synthetic manipulations were performed under a nitrogen atmosphere using standard Schlenk techniques. The previously known *P,P = E* ligands **a**, **b**, and **c**, were prepared according to the published methods [33] and characterization data were in accord with those previously reported [Pd(dimethylaminoethylnaphthyl-*C,N*)Cl]$_2$ (**3**) and [Pt(dimethylaminoethylnaphthyl-*C,N*)Cl]$_2$ (**4**) were prepared according to literature precedent [27,34]. NMR spectra were recorded on Bruker 400 or 500 MHz instruments and the chemical shifts reported in ppm relative to TMS, phosphoric acid or dimethyl selenide *via* reference to solvent resonances and correlation with Ξ values [35,36]. The ^{1}H and ^{13}C shifts were referenced to TMS *via* reference to the solvent. Selenium-77 couplings were also evaluated with a sample enriched in ^{77}Se for accuracy. The ^{77}Se couplings could be readily observed in natural abundance in the ^{31}P spectra, but required enrichment to be located in the ^{13}C spectra.

6.1. General procedure for preparation of [(κ^2-dman-C,N)M(κ^2-L)] SbF_6

The [(κ^2-*dman-C,N*)M]$_2$ dimer, **3** or **4**, (0.0300 mmol), the ligand (0.0600 mmol) and an excess of sodium hexafluoroantimonate (0.0473 g, 0.183 mmol) were combined in a flask prior to the addition of 7 mL of methylene chloride. After stirring for 18 h, the solution was filtered through Celite to remove insoluble material and the solvent was removed under vacuum. The complexes were recrystallized from methylene chloride/diethyl ether.

6.2. NMR data and analyses

6.2.1. [(κ^2-dman-C,N)Pd(dppmSe)]SbF_6 (**1a**)

^{1}H NMR (500 MHz, CD_2Cl_2) δ: 7.93 (ddd, J = 12.4, 7.3, 1.0 Hz, 2H, arom.), 7.71–7.13 (m, 22H, arom.), 6.93 (d, J = 8.6 Hz, 1H, arom.), 6.54 (dd, J = 8.6, 7.1 Hz, 1H, arom.), 4.60 (ddd, $J_{H,H}$ = 14.5, $J_{H,P}$ = 11.4, 9.3 Hz, $J_{H,Se}$ = 2.4 Hz, 1H, CH_2), 4.52 (dq, J = 6.3, 6.1 Hz, 1H, CHCH$_3$), 4.12 (ddd, $J_{H,H}$ = 14.5, $J_{H,P}$ = 14.5, 9.8 Hz, 1H, CH_2), 3.19 (d, $J_{H,H}$ = 3.5 Hz, $J_{H,Se}$ = 7.3 Hz 3H, NCH_3), 3.01 (d, J = 1.6 Hz, 3H, NCH_3), 2.02 (d, J = 6.3 Hz, 3H, CCH_3). ^{31}P NMR (202 MHz, CD_2Cl_2) δ 36.44 (d, $J_{P,P}$ = 34.0 Hz, $J_{P,Se}$ = 5.7 Hz), 30.47 (d, $J_{P,P}$ = 34.0 Hz, $J_{P,Se}$ = 571.5 Hz). ^{13}C NMR (125 MHz, CD_2Cl_2) δ [selected resonances] 153.19 (dd, $J_{C,P}$ = 2.6, 2.6 Hz, $J_{C,Se}$ = 30.7 Hz, *NapthC*-Pd), 149.50 (d, $J_{C,P}$ = 2.3 Hz, 1C, *Napth*), 135.92 (d, $J_{C,P}$ = 2.3 Hz, 1C, arom.), 134.68 (d, $J_{C,P}$ = 14.0 Hz, $J_{C,Se}$ = 3.6 Hz, *Napth*), 134.20–123.66, (arom.),130.13 (s, $J_{C,Se}$ = 3.6 Hz, *Napth*), 126.13 (d, $J_{C,P}$ = 5.6 Hz, $J_{C,Se}$ = 2.5 Hz, *Napth*), 74.54 (d, $J_{C,P}$ = 2.6 Hz *C*HCH$_3$), 53.00 (d, $J_{C,P}$ = 3.0 Hz NCH$_3$), 52.01 (dd, $J_{C,P}$ = 2.0, 2.0 Hz, $J_{C,Se}$ = 21.9 Hz NCH$_3$), 45.27 (dd, $J_{C,P}$ = 45.4, 24.4 Hz, $J_{C,Se}$ = 5.8 Hz *C*H$_2$), 24.57 (s, C*C*H$_3$). ^{77}Se NMR (95 MHz, CD_2Cl_2) −116.0 (d, $J_{Se,P}$ = 572 Hz). *Anal. Calcd* for $C_{39}H_{38}F_6NP_2PdSbSe$: C, 46.66; H, 3.82; N, 1.40%. Found: C, 46.85; H, 3.91; N, 1.40%.

6.2.2. [(κ^2-dman-C,N) Pt(dppmSe)]SbF_6 (**2a**)

^{1}H NMR (500 MHz, CD_2Cl_2) δ: 7.93 (dd, J = 12.6, 8.0 Hz, 2H, arom.), 7870–7.30 (m, 22H, arom.), 6.94 (d, J = 8.6 Hz, 1H, arom.), 6.73 (dd, J = 8.6, 3.5 Hz, $J_{H,Se}$ = 2.1 Hz, $J_{H,Pt}$ = 50.1 Hz br, 1H, arom.), 4.80 (dq, J = 6.2, 6.1 Hz, $J_{H,Pt}$ = ~50 Hz br, 1H, CHCH$_3$), 4.27 (ddd, $J_{H,H}$ = 10.8, $J_{H,P}$ = 6.1, 4.8 Hz, $J_{H,Se}$ ~ 0.5 Hz, 1H, CH_2), 3.89 (ddd, $J_{H,H}$ = 10.8, $J_{H,P}$ = 8.0, 4.0 Hz, $J_{H,Se}$ = 7.3 Hz, 1H, CH_2), 3.06 (d, J = 1.8 Hz, 3H, NCH_3), 2.92 (d, J = 1.6 Hz, 3H, NCH_3), 1.92 (d, J = 6.3 Hz, 3H, CCH_3). ^{31}P NMR (202 MHz, CD_2Cl_2) δ *trans* 30.42 (d, $J_{P,P}$ = 25.9 Hz, $J_{P,Se}$ = 549.0 Hz $J_{P,Pt}$ ~ 10 Hz P*(V)*), 17.02 (d, $J_{P,P}$ = 25.9 Hz, $J_{P,Se}$ = 5.4 Hz, $J_{P,Pt}$ = 4014.8 Hz P*(III)*); *cis* 36.10 (d, $J_{P,P}$ = 68.0 Hz, $J_{P,Se}$ = 521.0 Hz $J_{P,Pt}$ = 136.4 Hz P*(V)*,), 28.36 (d, $J_{P,P}$ = 68.0 Hz, $J_{P,Se}$ = 4.1 Hz, $J_{P,Pt}$ = 2013.5 Hz P*(III)*). ^{13}C NMR (125 MHz, CD_2Cl_2) δ *trans* [selected resonances] 148.17 (s, 1C, *Napth*), 142.67 (dd, $J_{C,P}$ = 2.5, 5.1 Hz, $J_{C,Se}$ = 28.1 Hz, 1C, *Napth*), 135.75, (d, $J_{C,P}$ = 3.0 Hz, arom.), 134.88, (d, $J_{C,P}$ = 8.4 Hz, $J_{C,Se}$ = 5.3 Hz *Napth*), 134.25–122.55, (arom.), 75.71 (d, $J_{C,P}$ = 3.0 Hz, $J_{C,Pt}$ ~ 42 Hz, *C*HCH$_3$), 54.12 (d $J_{C,P}$ = 3.1 Hz NCH$_3$), 52.68 (br s, $J_{C,Se}$ = 22.8 Hz NCH$_3$), 44.13 (dd, $J_{C,P}$ = 46.0, 32.7 Hz, $J_{C,Se}$ = 5.0 Hz, *C*H$_2$), 23.32 (s, C*C*H$_3$). δ *cis* [selected resonances] 150.38 (dd, $J_{C,P}$ = 111.9, 10.2 Hz *NapthC*-Pt), 149.82 (s, *Napth*), 135.50–122.55 (arom.), 79.16 (d, $J_{C,P}$ = 10.4 Hz *C*HCH$_3$), 55.56 (s, NCH$_3$), 52.82 (d $J_{C,P}$ = 4.6 Hz NCH$_3$), 39.29 (dd, $J_{C,P}$ = 46.8, 22.4 Hz, $J_{C,Se}$ = 5.5 Hz, *C*H$_2$), 23.63 (s, C*C*H$_3$). ^{77}Se NMR (95 MHz) δ *trans* −107.0 (d, $J_{P,Se}$ = 549 Hz, $J_{Se,Pt}$ = 363 Hz); *cis* −51.0 (d, $J_{P,Se}$ = 521 Hz, $J_{Se,Pt}$ = 265 Hz). *Anal. Calcd* for $C_{39}H_{38}F_6NP_2PtSbSe\cdot C_4H_{10}O$: C, 44.27; H, 4.15; N, 1.20%. Found: C, 44.40; H, 3.78; N, 1.42%.

6.2.3. [(κ^2-dman-C,N)Pd(dppmS)]SbF_6 (**1b**)

^{1}H NMR (500 MHz, CD_2Cl_2) δ: 7.25 (ddd, J = 12.5, 8.5, 1.3 Hz, 2H, arom.), 7.81–7.30 (m, 22H, arom.), 6.95 (d, J = 8.7 Hz, 1H, arom.), 6.57 (dd, J = 8.6, 7.0 Hz, 1H, arom.), 4.55 (dq, J = 6.2, 6.1 Hz, 1H, CHCH$_3$), 4.20 (ddd, $J_{H,H}$ = 13.2, $J_{H,P}$ = 8.8, 8.5 Hz, 1H, CH_2), 4.03 (ddd, $J_{H,H}$ = 13.2, $J_{H,P}$ = 8.9, 8.5 Hz, 1H, CH_2), 3.21 (d, J = 3.7 Hz, 3H, NCH_3), 3.03 (d, J = 1.6 Hz, 3H, NCH_3), 2.00 (d, J = 6.3 Hz, 3H, CCH_3). ^{31}P NMR (202 MHz, CD_2Cl_2) δ 47.20 (d, $J_{P,P}$ = 30.3 Hz), 34.22 (d, J_{PP} = 30.3 Hz). *Anal. Calcd* for $C_{39}H_{38}F_6NP_2PdSbS$ $0.5C_4H_{10}O$: C, 50.04; H, 4.50; N, 1.39%. Found: C, 50.32; H, 4.48; N, 1.52%.

6.2.4. [(κ^2-dman-C,N)Pt(dppmS)]SbF_6 (**2b**)

^{1}H NMR (400 MHz, CD_2Cl_2) δ: 7.93 (ddd, J = 12.6, 7.2, 1.3 Hz, 2H, arom.), 7.77–7.30 (m, 22H, arom.), 6.94 (d, J = 8.5 Hz, 1H, arom.),

6.72 (dd, $J = 8.5$, 3.0 Hz, $J_{H,Pt} = 54.3$ Hz, 1H, arom.), 4.79 (dq, $J = 6.4$, 6.0 Hz, $J_{H,Pt} = 53.5$ Hz, 1H, C*H*CH$_3$), 4.27 (ddd, $J_{H,H} = 10.8$, $J_{H,P} = 8.4$, 6.2 Hz, $J_{H,Pt} = 64.9$ Hz, 1H, CH_2), 3.88 (ddd, $J_{H,H} = 10.8$, $J_{H,P} = 10.4$, 5.3 Hz, $J_{H,Pt}$ nr, 1H, CH_2), 3.54 (d, $J = 3.5$ Hz, $J_{H,Pt} = 19.8$ Hz, 3H, NCH_3), 3.06 (d, $J = 1.6$ Hz, $J_{H,Pt} = 29.8$ Hz, 3H, NCH_3), 1.91 (d, $J = 6.3$ Hz, 3H, CCH_3). ^{31}P NMR (162 MHz, CD_2Cl_2) δ *trans* 49.02 (d, $J_{P,P} = 23.0$ Hz, $J_{P,Pt} \sim 11$ Hz P*(V)*), 14.78 (d, $J_{P,P} = 23.0$ Hz, $J_{P,Pt} = 4000.2$ Hz P*(III)*); *cis* 56.55 (d, $J_{P,P} = 63.1$ Hz, $J_{P,Pt} = 135$ Hz P*(V)*,), 24.93 (d, $J_{P,P} = 63.1$ Hz, $J_{P,Pt} = 1965.2$ Hz P*(III)*); *Anal. Calcd* for $C_{39}H_{38}F_6NP_2PtSbS\ H_2O$: C, 44.10; H, 3.79; N, 1.30%. Found: C, 43.92; H, 3.87; N, 1.29%.

*6.2.5. [(κ^2-dman-C,N)Pd(dppmO)]SbF_6 (**1c**)*

^{1}H NMR (500 MHz, CD_2Cl_2) δ: 7.84 (ddd, $J = 12.7$, 8.1, 1.1 Hz, 2H, arom.), 7.71–7.13 (m, 22H, arom.), 7.03 (d, $J = 8.5$ Hz, 1H, arom.), 6.52 (dd, $J = 8.5$, 6.3 Hz, 1H, arom.), 4.56 (dq, $J = 6.3$, 6.1 Hz, 1H, C*H*CH$_3$), 3.68 (ddd, $J_{H,H} = 11.0$, $J_{H,P} = 6.8$, 5 Hz, 1H, CH_2), 3.64 (ddd, $J_{H,H} = 11.0$, $J_{H,P} = 8.0$, 6.50 Hz, 1H, CH_2), 3.09 (d, $J = 3.6$ Hz, 3H, NCH_3), 3.05 (d, $J = 1.6$ Hz, 3H, NCH_3), 1.98 (d, $J = 6.4$ Hz, 3H, CCH_3). ^{31}P NMR (202 MHz, CD_2Cl_2) δ 52.80 (d, $J_{P,P} = 17.8$ Hz, 1P,), 27.93 (d, $J_{PP} = 17.8$ Hz). *Anal. Calcd* for $C_{39}H_{38}F_6NP_2PdSbO$: C, 49.79; H, 4.07; N, 1.49%. Found: C, 49.42; H, 4.12; N, 1.45%.

*6.2.6. [(κ^2-dman-C,N)Pt(dppmO)]SbF_6 (**2c**)*

^{1}H NMR (400 MHz, CD_2Cl_2) δ: *trans* 7.91 (ddd, $J = 12.6$, 7.2, 1.1 Hz, 2H, arom.), 7.80–7.31 (m, 22H, arom.), 6.98 (d, $J = 8.6$ Hz, 1H, arom.), 6.63 (dd, $J = 8.5$, 2.9 Hz, $J_{H,Pt} = 66.3$ Hz, 1H, arom.), 4.86 (dq, $J = 6.3$, 6.0 Hz, $J_{H,Pt} = 61.7$ Hz, 1H, C*H*CH$_3$), 3.65 (ddd, $J_{H,H} = 10.7$, $J_{H,P} = 6.3$, 3.8 Hz, 1H, CH_2), 3.53 (ddd, $J_{H,H} = 10.7$, $J_{H,P} = 8.1$, 4.5 Hz, 1H, CH_2), 3.35 (d, $J = 3.1$ Hz, 3H, NCH_3), 3.08 (d, $J = 1.6$ Hz, $J_{H,Pt} = 26.6$ Hz, 3H, NCH_3), 1.91 (d, $J = 6.3$ Hz, 3H, CCH_3). ^{31}P NMR (162 MHz, CD_2Cl_2) δ *trans* 60.25 (d, $J_{P,P} = 10.8$ Hz, $J_{P,Pt}$ = not observed, *P(V)*), 11.27 (d, $J_{P,P} = 10.8$ Hz, $J_{P,Pt} = 4064.7$ Hz, *P(III)*) *cis* 73.22 (d, $J_{P,P} = 33.2$ Hz, $J_{P,Pt} \sim 120$ Hz, *P(V)*), 22.09 (d, $J_{P,P} = 34.1$ Hz, $J_{P,Pt} = 1900.5$ Hz, *P(III)*). *Anal. Calcd* for $C_{39}H_{38}F_6NP_2PtSbO$: C, 45.50; H, 3.72; N, 1.36%. Found: C, 45.38; H, 3.68; N, 1.44%.

6.2.7. ^{31}P NMR spectra of free ligands

*6.2.7.1. dppmSe (**a**).* ^{31}P NMR (202 MHz, CD_2Cl_2) δ 30.75 (d, $J_{P,P} = 85.6$ Hz), −27.52 (d, $J_{P,P} = 85.6$ Hz, $J_{P,Se} = 732.0$ Hz). ^{77}Se NMR (95 MHz, CD_2Cl_2) −292.5 (dd, $^1J_{Se,P} = 732$ Hz, $^3J_{Se,P} = 13$ Hz).

*6.2.7.2. dppmS (**b**).* ^{31}P NMR (162 MHz, CD_2Cl_2) δ 39.96 (d, $J_{P,P} = 77.2$ Hz), −28.44 (d, $J_{P,P} = 77.2$ Hz).

*6.2.7.3. dppmO (**c**).* ^{31}P NMR (162 MHz, CD_2Cl_2) δ 27.76 (d, $J_{P,P} = 50.1$ Hz), −28.62 (d, $J_{P,P} = 50.1$ Hz).

*6.2.8. Treatment of **1c** and **2c** with 3,5-lutidine*

*6.2.8.1. [**1c** + 0.5 eq lutidine].* ^{31}P NMR (−70 °C) ^{31}P NMR (202 MHz, CD_2Cl_2) δ 52.11 (d, $J_{P,P} = 18.0$ Hz, κ^2-*P(V)*), 26.83 (d, $J_{P,P} = 18.0$ Hz, $J_{P,Pt} = 4145$ Hz, κ^2-*P(III)*); δ 31.11 (s, br, κ^1-*P(V)*), 24.34 (s, br, κ^1-*P(III)*).

*6.2.8.2. [**2c** + 0.5 eq lutidine].* ^{31}P NMR ^{31}P NMR (202 MHz, CD_2Cl_2) δ 62.24 (d, $J_{P,P} = 10.6$ Hz, κ^2-*P(V)*), 11.19 (d, $J_{P,P} = 10.6$ Hz, $J_{P,Pt} = 4145.0$ Hz, κ^2-*P(III)*); δ 25.22 (d, $J_{P,P}$ = nr, $J_{P,Pt} \sim 54$ Hz κ^1-*P(V)*), 7.42 (d, $J_{P,P}$ = nr, $J_{P,Pt} = 4072$ Hz, κ^1-*P(III)*).

6.3. X-ray crystallography

All of the measurements were made on a Rigaku CCD SCXmini diffractometer using monochromated Mo-Kα radiation. Data are summarized in Table 5. The structure was solved by direct methods [37] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. Full-matrix least squares refinement on F^2 was used. Calculations were performed using the Crystal Structure crystallographic software package [38] except for refinement, which was performed using SHELXL-97 [39]. Both **2a** and **2c** crystallized in the orthorhombic space group $P2_12_12_1$. The cell for **2a** also included four molecules of methylene chloride. The cell for **2c** included two molecules of methylene chloride and showed a disorder of two orientations of the hexafluoroantimonate.

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Appendix A. Supplementary data

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 784352 and 784353 for compounds **2a** and **2c**. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK; Fax. (int code) +44 (1223)336 033; or Email: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk.

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