

MIXED LIGAND COMPLEXES OF ZEROVALENT PLATINUM, PALLADIUM AND NICKEL CONTAINING A CHELATING OLEFINIC TERTIARY PHOSPHINE *

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Summary

The potentially chelating ligand (2-vinylphenyl)diphenylphosphine, $o\text{-CH}_2=\text{CHC}_6\text{H}_4\text{PPh}_2(\text{SP})$ reacts either with $\text{M}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$ ($\text{M} = \text{Pt}, \text{Pd}, \text{Ni}$), or with $\text{M}(\text{1,5-COD})_2$ ($\text{M} = \text{Pt}, \text{Ni}$) and triphenylphosphine in a 1/2 mol ratio, to give mixed ligand complexes $\text{M}(\text{PPh}_3)_2(\text{SP})$. The platinum and palladium compounds can be isolated, whereas the nickel compound has been identified in solution by ^1H and ^{31}P NMR spectroscopy. All the complexes disproportionate readily, the palladium complex immediately on dissolution giving $\text{Pd}(\text{PPh}_3)(\text{SP})_2$ and $\text{Pd}(\text{PPh}_3)_3$, the platinum and nickel complexes more slowly in solution to $\text{M}(\text{SP})_2$, $\text{M}(\text{PPh}_3)_3$ and PPh_3 . The platinum and nickel complexes contain bidentate SP and are probably tetrahedral, whereas $\text{Pd}(\text{PPh}_3)_2(\text{SP})$ in the solid state has a free vinyl group. In contrast to $\text{Ni}(\text{PPh}_3)_2(\text{SP})$, $\text{Pt}(\text{PPh}_3)_2(\text{SP})$ undergoes an intramolecular process in solution, probably one-ended dissociation of the vinyl group, which equivalences the triphenylphosphine ligands; this process can be frozen at -117°C . Both $\text{Ni}(\text{PPh}_3)_2(\text{SP})$ and $\text{Pt}(\text{PPh}_3)_2(\text{SP})$ undergo intermolecular ligand exchange, above -50°C in the case of platinum, above -30°C in the case of nickel; the triphenylphosphine ligands of $\text{Ni}(\text{PPh}_3)_2(\text{SP})$ exchange at different rates. The results can be correlated with the trend in equilibrium constants for the reaction $\text{M}(\text{PPh}_3)_3 + \text{C}_2\text{H}_4 \rightleftharpoons \text{M}(\text{PPh}_3)_2(\text{C}_2\text{H}_4) + \text{PPh}_3$ ($\text{M} = \text{Ni} > \text{Pt} > \text{Pd}$).

Introduction

The triad of d^{10} zerovalent transition metals, nickel(0), palladium(0) and platinum(0), forms a range of stable complexes both with tertiary phosphines and with monodentate and multidentate olefins [1–6]. The coordination number of the

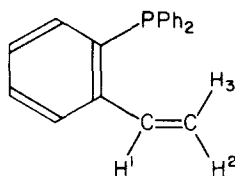
* Dedicated to Professor Lamberto Malatesta in recognition of his important contributions to organometallic chemistry.

metal atom in these complexes varies from two to four, the lower coordination numbers being favoured by bulky ligands. Some tertiary phosphines form isolable complexes of these metals having different coordination numbers, e.g. $\text{Pt}(\text{PPh}_3)_3$, $\text{Pt}(\text{PPh}_3)_4$ [7,8], $\text{Ni}(\text{PPh}_3)_3$, $\text{Ni}(\text{PPh}_3)_4$ [9–12] and $\text{Pt}(\text{P-}i\text{-Pr}_3)_2$, $\text{Pt}(\text{P-}i\text{-Pr}_3)_3$ [13], and the equilibria between the various species have been studied by variable temperature ^{31}P NMR spectroscopy [12,14–16]. There are also many complexes of the three elements that contain both tertiary phosphines and olefins, exemplified by $\text{M}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$ and $\text{M}(\text{PCy}_3)(\text{C}_2\text{H}_4)_2$ [2–6]. Tolman and co-workers [11] have compared the binding abilities of triarylphosphines and ethylene for the three metals by measuring the equilibrium constants in benzene at 25°C for reaction 1 and find them to vary in the order $\text{Ni} \gg \text{Pt} > \text{Pd}$.



In the case of $\text{M} = \text{Pt}$ and $\text{L} = \text{PPh}_3$, the equilibrium can be driven to the right at -100°C owing to the formation of ML_4 [16].

Another way of making the comparison is to examine the complexes with nickel(0), palladium(0) and platinum(0) formed by the potentially chelating olefinic tertiary phosphine (2-vinylphenyl)diphenylphosphine (*o*-styryldiphenylphosphine, $o\text{-CH}_2=\text{CHC}_6\text{H}_4\text{PPh}_2$ (I), abbreviated SP), which forms stable chelate olefin complexes with many transition elements [17]. We have isolated complexes of formula



I(SP)

$\text{M}(\text{SP})_2$ ($\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$) and have established that the nickel(0) and platinum(0) complexes are tetrahedral, with both vinyl groups coordinated, whereas the palladium(0) complex in the solid state is approximately trigonal, one vinyl group being coordinated and the other free [18]. In this paper we discuss mixed ligand complexes of the type $\text{M}(\text{PPh}_3)_2(\text{SP})$.

Results

(1) *Platinum.* Reaction of $\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$ with SP in a 1/1 mol ratio, or treatment of $\text{Pt}(\text{1,5-COD})_2^*$ with two equivalents of triphenylphosphine and one equivalent of SP at room temperature, gives a bright yellow, moderately air-sensitive complex of empirical formula $\text{Pt}(\text{PPh}_3)_2(\text{SP})$. The ^{31}P NMR spectrum of this compound indicates that it is monomeric, although an osmometric molecular weight determination in toluene at 37°C gave a value about half of that expected for a monomer, probably as a result of disproportionation and oxidation (see below). The

* Abbreviations: 1,5-COD = cycloocta-1,5-diene; Cy = cyclohexyl; dppe = 1,2-bis(diphenylphosphino)ethane, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$

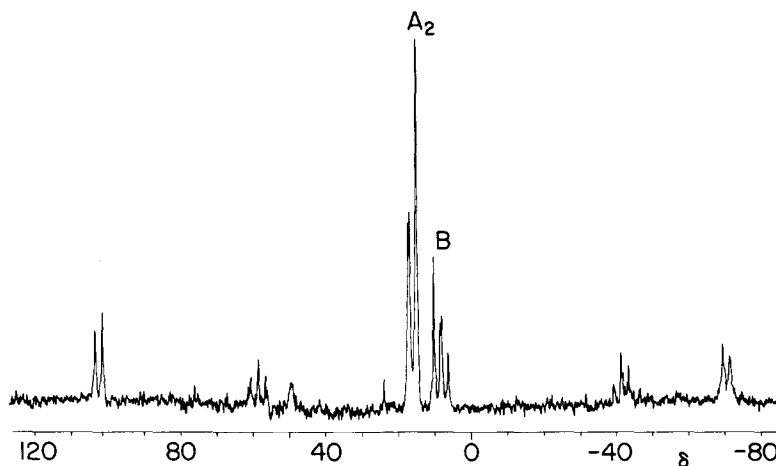


Fig. 1. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (24.28 MHz) of $\text{Pt}(\text{PPh}_3)_2(\text{SP})$ at -70°C in toluene- d_8 /toluene.

IR spectrum in a KBr disc shows no $\nu(\text{C}=\text{C})$ band in the 1620 cm^{-1} region, suggesting that the vinyl group of SP is coordinated.

Both ^1H and ^{31}P NMR spectra show the complex to be fluxional. At room temperature, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum in toluene consists of two broad resonances without ^{195}Pt satellites at δ 23 and 17 ppm relative to 85% H_3PO_4 . On cooling to -30°C , a seven-line pattern accompanied by ^{195}Pt satellites appears and this sharpens as the temperature is lowered to -70°C (Fig. 1). Analysis of this spectrum as an A_2BX ($\text{X} = ^{195}\text{Pt}$) spin system gives the following parameters: $\delta(\text{P}_\text{A})$ 16.5, $\delta(\text{P}_\text{B})$ 8.1, $^2J(\text{P}_\text{A}\text{P}_\text{B})$ 50, $^1J(\text{PtP}_\text{A})$ 4209, $^1J(\text{PtP}_\text{B})$ 2411 (coupling constants in Hz). On cooling a solution in $\text{THF-}d_8$ to -90°C , this pattern broadens again and sharpens at -117°C to an eleven-line pattern, also with ^{195}Pt satellites (Fig. 2). This

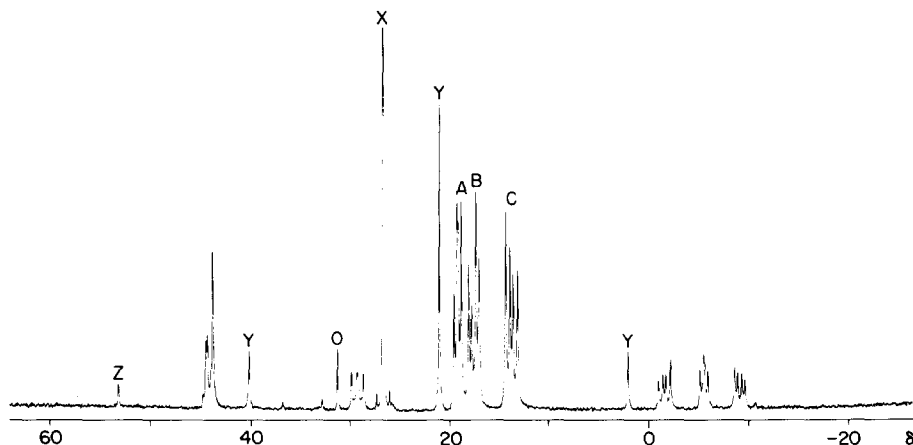
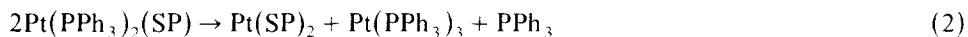


Fig. 2. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (80.98 MHz) of $\text{Pt}(\text{PPh}_3)_2(\text{SP})$ at -117°C in $\text{THF-}d_8$. Peaks marked X, Y and Z are probably due to Ph_3PO , $\text{Pt}(\text{SP})_2$ and $\text{Pt}(\text{PPh}_3)_3$ respectively; O arises from an unknown impurity.

more complex spectrum can be analysed as an ABCX spin system ($X = {}^{195}\text{Pt}$) to give the following parameters: $\delta(\text{P}_\text{A})$ 19.3, $\delta(\text{P}_\text{B})$ 17.6, $\delta(\text{P}_\text{C})$ 13.9, ${}^2J(\text{P}_\text{A}\text{P}_\text{B})$ 26.8, ${}^2J(\text{P}_\text{A}\text{P}_\text{C})$ 34.5, ${}^2J(\text{P}_\text{B}\text{P}_\text{C})$ 61.0, ${}^1J(\text{PtP}_\text{A})$ 4009, ${}^1J(\text{PtP}_\text{B})$ 4305, ${}^1J(\text{PtP}_\text{C})$ 2501. The peaks due to P_A and P_B in the spectrum at -117°C are assigned tentatively to the two triphenylphosphine ligands and the peak due to P_C is due to the phosphorus atom of the SP ligand. At -50°C P_A and P_B are equivalent on the NMR time scale. The ${}^{31}\text{P}$ chemical shifts vary markedly with temperature and with solvent, so the chemical shift of P_A and P_B undergoing averaging at -70°C is not the mean of the individual chemical shifts at -117°C .

The ${}^{31}\text{P}\{^1\text{H}\}$ NMR spectrum in $\text{THF}-d_8$ at -117°C also shows peaks at δ 21.1 ppm (${}^1J(\text{PtP})$ 3106 Hz), at δ 53.0 and 26.6 ppm, the last two having no ${}^{195}\text{Pt}$ satellites. The first is almost certainly due to $\text{Pt}(\text{SP})_2$, although the chemical shift and coupling constant differ slightly from those of the authentic material measured in toluene at room temperature (δ 17.6 ppm, ${}^1J(\text{PtP})$ 3130 Hz) [18]. The second peak is probably due to $\text{Pt}(\text{PPh}_3)_3$ (δ 55 ppm, ${}^1J(\text{PtP})$ 4370 Hz in toluene at -50°C [11], δ 49.9 ppm, ${}^1J(\text{PtP})$ 4438 Hz in toluene at -70°C [16]), the ${}^{195}\text{Pt}$ satellites being absent owing to exchange with triphenylphosphine liberated in the disproportionation reaction (eq. 2):



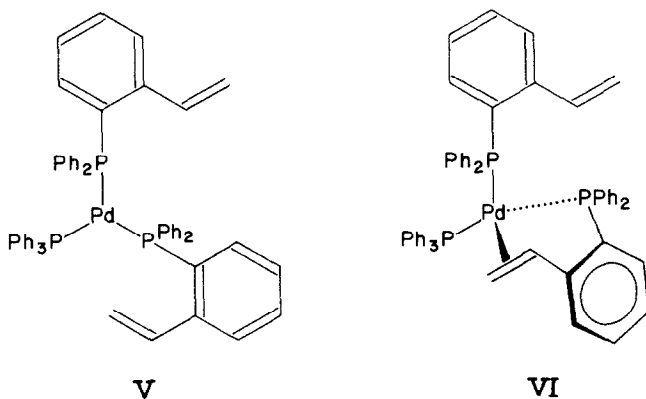
This reaction occurs completely within a week in toluene but is much more rapid in THF. The peak at δ 26.6 ppm is assigned to triphenylphosphine oxide (literature values for its ${}^{31}\text{P}$ chemical shift range from 23–27 ppm [19]). This is probably formed by aerial oxidation of the liberated triphenylphosphine, a process which is catalysed by $\text{M}(\text{PPh}_3)_3$ complexes [20,21].

The ${}^1\text{H}$ NMR spectrum of $\text{Pt}(\text{PPh}_3)_2(\text{SP})$ in toluene- d_8 at room temperature is broad but at -50°C there appear two sets of vinyl proton resonances, each with ${}^{195}\text{Pt}$ satellites, in a ratio of ca. 5/1. After ${}^{31}\text{P}$ -decoupling, the resonances of the major component, $\text{Pt}(\text{PPh}_3)_2(\text{SP})$, are a doublet of doublets at δ 4.85 ppm due to H^1 and a pair of doublets at δ 3.93 ppm and δ 2.83 ppm due to H^2 and H^3 respectively (J_{13} 10.7 Hz, J_{12} 8.7 Hz, $J(\text{PtH}^1)$ 52 Hz, $J(\text{PtH}^2)$ 60 Hz, $J(\text{PtH}^3)$ 40 Hz). The upfield shift of the vinyl resonances in $\text{Pt}(\text{PPh}_3)_2(\text{SP})$ relative to those of the free ligand confirms that the vinyl group is coordinated and the Pt–H coupling constants are similar in magnitude to those observed in other olefin-platinum(0) complexes, e.g. $J(\text{PtH})$ 55 Hz for $\text{Pt}(1,5\text{-COD})_2$ [22]. The corresponding resonances of the minor component are at δ 4.05(dd), 3.33(d) and 2.47(d) ppm and are assigned to $\text{Pt}(\text{SP})_2$ formed by disproportionation.

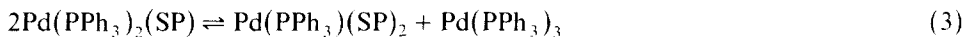
The spectroscopic data show that $\text{Pt}(\text{PPh}_3)_2(\text{SP})$ is a tetrahedrally coordinated complex containing bidentate SP. Because the chelate ring of SP is non-planar, the triphenylphosphine ligands should be inequivalent, as is observed at -117°C . In principle, one can envisage four limiting configurations for the complex, shown in Fig. 3. In two of these, I and III, the coordinated vinyl group is in a plane approximately at right-angles to one of the Pt– PPh_3 bonds (Pt– L_A in Fig. 3) and approximately parallel to the other Pt– PPh_3 bond (Pt– L_B). In II and IV, the vinyl group is parallel to Pt– L_A and at right-angles to Pt– L_B . Configurations I and II are related by chelate ring inversion, as are III and IV; however, I and III can only be interconverted by one-ended dissociation of the vinyl group, thus allowing the other face of the olefin to coordinate. The same is true for II and IV.

Fig. 3. Possible configurations of $\text{Pt}(\text{PPh}_3)_7(\text{SP})$.

(2) *Palladium.* Reaction of $\text{Pd}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$ with one equivalent of SP in toluene at -70°C gives a pale yellow solid of empirical formula $\text{Pd}(\text{PPh}_3)_2(\text{SP})$. Like its platinum analogue, the palladium compound has a molecular weight in toluene which is about half the formula weight. The IR spectrum in a KBr disc shows a weak band at 1620 cm^{-1} , suggesting that $\text{Pd}(\text{PPh}_3)_2(\text{SP})$, unlike $\text{Pt}(\text{PPh}_3)_2(\text{SP})$, contains one or more free vinyl groups. The ^1H NMR spectrum in toluene- d_8 at -60°C shows three broad resonances at δ ca. 5.9, 4.2 and 3.7 ppm attributable to coordinated vinyl groups; these signals broaden further on warming to room temperature. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows that there are two species present in solution. At room temperature, there is a singlet at δ 22.5 ppm and a less intense, broad resonance at δ 12.5 ppm. On cooling to -70°C , the former remains essentially unchanged, while the latter resolves into a sharp A_2X pattern consisting of a doublet at δ 26.2 ppm and a triplet at δ 4.2 ppm ($^2J(\text{P}_\text{A}\text{P}_\text{X})$ 36 Hz). The singlet at δ 22.6 ppm is assigned on the basis of its chemical shift to $\text{Pd}(\text{PPh}_3)_3$ (lit. [14] δ_P 22.6 ppm in toluene at -70°C). Since peaks due to $\text{Pd}(\text{SP})_2$ and $\text{Pd}(\text{SP})_3$ [18] are



not observed, the second species must be $\text{Pd}(\text{PPh}_3)(\text{SP})_2$, formed by rapid disproportionation of $\text{Pd}(\text{PPh}_3)_2(\text{SP})$ (eq. 3).



The available data are not sufficient to define the structure of $\text{Pd}(\text{PPh}_3)(\text{SP})_2$. The two most likely possibilities are trigonal planar, with two free vinyl groups (V), and tetrahedral, with one coordinated and one free vinyl group (VI). If the latter is correct, the fact that the olefin ^1H resonances are broad even at -90°C , where the ^{31}P resonances are sharp, suggests that there may be fast intramolecular exchange between the free and coordinated vinyl groups.

(3) *Nickel.* Reaction of $\text{Ni}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$ with one equivalent of SP in toluene at room temperature gives a very air-sensitive solution from which an orange solid is precipitated by hexane. Although the H, P and Ni analyses are in reasonable agreement with the formulation $\text{Ni}(\text{PPh}_3)_2(\text{SP})$, the carbon analysis is ca. 7% too low (see Experimental). A solid of similar appearance and composition is obtained by addition of two equivalents of triphenylphosphine and one equivalent of SP to $\text{Ni}(\text{COD})_2$ (1 equiv.) in toluene and subsequent precipitation with hexane. Its IR spectrum shows no $\nu(\text{C}=\text{C})$ absorption in the 1620 cm^{-1} region.

The NMR spectroscopic data show, with reasonable certainty, that the solid

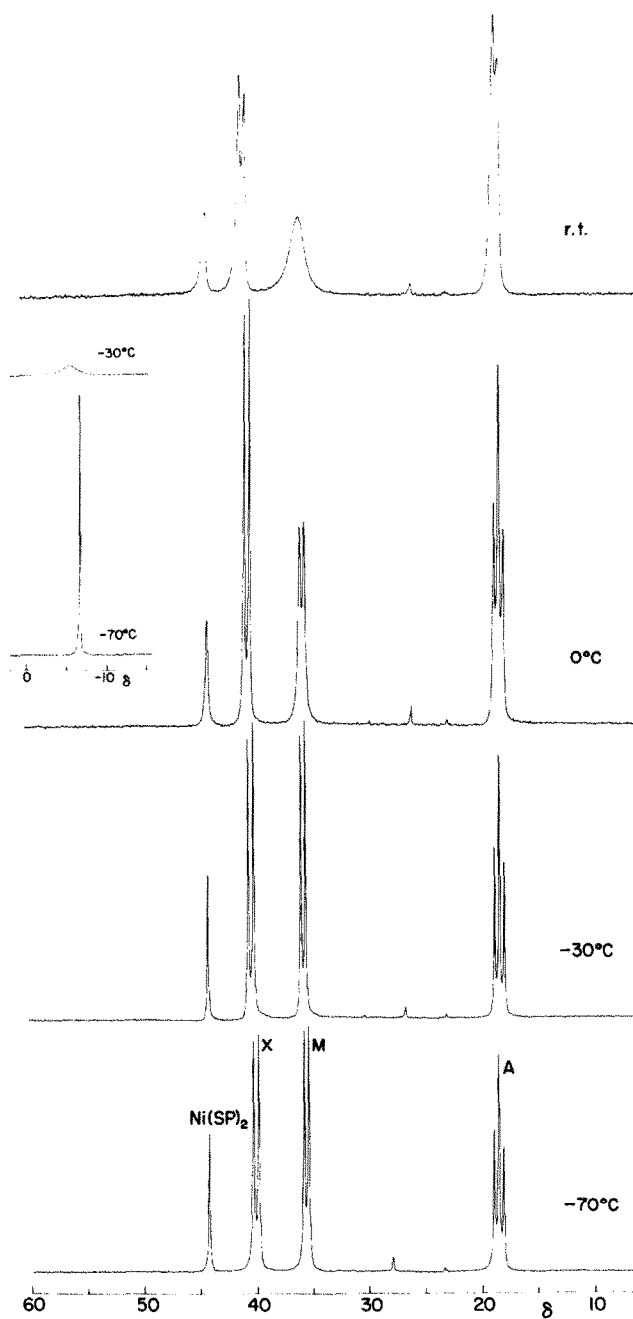


Fig. 4. Variable temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (80.98 MHz) of $\text{Ni}(\text{PPh}_3)_2(\text{SP})$ in toluene; the complex had been made in situ from $\text{Ni}(\text{COD})_2/2\text{PPh}_3/\text{SP}$. Insert shows peak due to PPh_3 undergoing exchange with $\text{Ni}(\text{PPh}_3)_2(\text{SP})$.

contains predominantly the desired compound $\text{Ni}(\text{PPh}_3)_2(\text{SP})$, together with variable amounts of $\text{Ni}(\text{SP})_2$, $\text{Ni}(\text{PPh}_3)_n$ ($n = 3$ or 4) and (2-vinylphenyl)diphenylphosphine oxide, $o\text{-CH}_2=\text{CHC}_6\text{H}_4\text{P}(\text{O})\text{Ph}_2$. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum in toluene at -70°C (Fig. 4) contains a pair of doublets at δ 40.0 ppm (P_X) and δ 35.5 ppm (P_M) and a doublet of doublets (almost a 1/2/1 triplet) at δ 18.4 ppm (P_A), the coupling constants $^2J(\text{P}_\text{A}\text{P}_\text{X})$ and $^2J(\text{P}_\text{A}\text{P}_\text{M})$ being 35.6 and 33.2 Hz, respectively. The signals in this first-order spectrum are assigned to the inequivalent ^{31}P nuclei of tetrahedral $\text{Ni}(\text{PPh}_3)_2(\text{SP})$, which is isostructural with the platinum compound. In addition, there are singlets whose relative intensity varies from sample to sample at δ 43.6, 28.9, 25.1 and -6.8 ppm. The first two of these are undoubtedly due to $\text{Ni}(\text{SP})_2$ and $\text{CH}_2=\text{CHC}_6\text{H}_4\text{P}(\text{O})\text{Ph}_2$, respectively, as evidenced by comparison with the spectra of authentic samples. The peak at δ 25.1 ppm is probably due to $\text{Ni}(\text{PPh}_3)_3$ or $\text{Ni}(\text{PPh}_3)_4$ in equilibrium with free triphenylphosphine, which is responsible for the peak at δ -6.8 ppm.

In the $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum at room temperature, the peaks due to the coordinated vinyl group of $\text{Ni}(\text{PPh}_3)_2(\text{SP})$ appear as a doublet of doublets at δ 4.55 ppm due to H^1 and a pair of doublets at δ 3.45 and 2.95 ppm due to H^2 and H^3 respectively (J_{13} 11.7 Hz, J_{12} 8.9 Hz). There is also an overlapping, less intense set of coordinated vinyl resonances at δ 4.45, 3.38 and 2.72 ppm due to $\text{Ni}(\text{SP})_2$ and a pair of doublets at δ 5.50 and 5.00 ppm (J 17.3, 11.0 Hz) which probably arise from H^2 and H^3 in the phosphine oxide, $o\text{-CH}_2=\text{CHC}_6\text{H}_4\text{P}(\text{O})\text{Ph}_2$.

If a solution containing $\text{Ni}(\text{COD})_2$ (1 equiv.) in toluene- d_8 is treated in situ with triphenylphosphine (2 equiv.) and SP (1 equiv.) and the ^{31}P NMR spectrum is recorded immediately at -70°C , the only peaks observed are the triplet and two doublets assigned to $\text{Ni}(\text{PPh}_3)_2(\text{SP})$, the other impurity peaks being either absent or of negligibly low intensity. Clearly disproportionation and adventitious oxidation occur during the subsequent work-up, these processes being even more rapid than in the case of $\text{Pt}(\text{PPh}_3)_2(\text{SP})$. The possibility that the triplet and two doublets are due to a complex $\text{Ni}(\text{SP})_2(\text{PPh}_3)$ containing one bidentate and one monodentate SP can be ruled out, because a solution prepared in situ from $\text{Ni}(\text{COD})_2$ (1 equiv.), SP (2 equiv.) and PPh_3 (1 equiv.) shows only a slightly broadened singlet at δ 38 ppm in its $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, the triplet/doublet/doublet pattern being almost completely absent. The singlet at δ 38 ppm also appears in the spectrum of a solution containing equimolar amounts of $\text{Ni}(\text{SP})_2$ and PPh_3 , the shift from the value for pure $\text{Ni}(\text{SP})_2$ (δ 42.5 ppm) being due to intermolecular exchange [18].

When a solution containing $\text{Ni}(\text{PPh}_3)_2(\text{SP})$ prepared in situ is allowed to warm from -70 to $+20^\circ\text{C}$, the doublet at δ 35.5 ppm (P_M) broadens; at the same time, the resonance at δ -6.8 ppm due to PPh_3 (either deliberately added or present in small amount as a result of disproportionation) disappears and the doublet of doublets at δ 18.4 ppm (P_A) changes to a broad doublet owing to loss of coupling with P_M (Fig. 4). From 20 to 35°C the doublets at δ 35.5 and 18.4 ppm also broaden. Finally, at 50°C , the lower field signals coalesce into a single broad peak and the highest field peak is a slightly broadened singlet.

If we make the reasonable assumption that P_M and P_X correspond to the PPh_3 ligands and that P_A corresponds to SP, then these spectra show that the inequivalent triphenylphosphine ligands undergo intermolecular exchange at different rates and only approach equivalence as a result of this exchange at ca. 50°C . The exchange undoubtedly involves dissociation of triphenylphosphine to give a three-coordinate

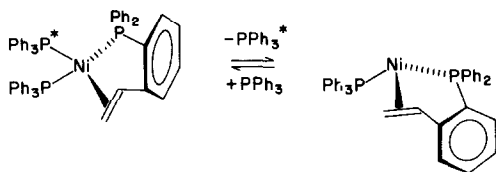
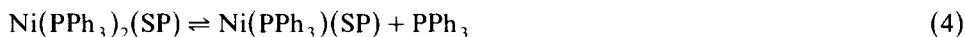


Fig. 5. Suggested mechanism of intermolecular exchange of coordinated PPh_3 in $\text{Ni}(\text{PPh}_3)_2(\text{SP})$.

complex containing bidentate SP (eq. 4):



One might have expected the three-coordinate intermediate $\text{Ni}(\text{PPh}_3)(\text{SP})$ to be trigonal planar, but if this were the case, intermolecular exchange should make the triphenylphosphine ligands of $\text{Ni}(\text{PPh}_3)_2(\text{SP})$ equivalent even at -70°C . We suggest that $\text{Ni}(\text{PPh}_3)(\text{SP})$ is sufficiently distorted from planarity that re-entry of triphenylphosphine occurs preferentially from one side of the molecule, so that the two triphenylphosphine ligands of $\text{Ni}(\text{PPh}_3)_2(\text{SP})$ exchange at different rates. The process is illustrated in Fig. 5. This hypothesis is supported by the observation that in the closely related complex $\text{Pd}(\text{SP})_2$, which in the solid state contains one monodentate P-bonded SP and one bidentate SP, the palladium atom lies $0.22 \text{ \AA}$ above the plane defined by the phosphorus atoms and the mid-point between the carbon atoms of the coordinated olefin; moreover, the coordinated olefin deviates by ca. 25° from the ideal trigonal plane [18]. Even in the more symmetrical complex $\text{Pt}(\text{PPh}_3)_3$, the platinum atom is reported to be situated $0.1 \text{ \AA}$ from the ideal trigonal plane [24].

Discussion

The spectroscopic data for the platinum(0) and nickel(0) complexes $\text{M}(\text{PPh}_3)_2(\text{SP})$ indicate that the metal atoms are tetrahedrally coordinated by two PPh_3 ligands and a bidentate SP ligand. An intriguing feature of $\text{Pt}(\text{PPh}_3)_2(\text{SP})$ is that while two of the $J(\text{PtP})$ values observed at -117°C are of the magnitude expected for a triarylphosphine-platinum(0) complex (ca. 4000 Hz) [25], the third is much smaller (ca. 2500 Hz) and is in fact the lowest recorded for such a complex. This low value is retained in the spectrum at -70°C while the two normal values approximately average, so the structure does not alter significantly in this temperature range. The spectroscopic behaviour of $\text{Pt}(\text{PPh}_3)_2(\text{SP})$ suggests (but does not absolutely prove) that the small $J(\text{PtP})$ value is associated with the phosphorus atom of SP, the magnitude being considerably less than in tetrahedral $\text{Pt}(\text{SP})_2$ (3130 Hz) [18]. This low value cannot be attributed to weak binding of the SP phosphorus atom, because the average $^2J(\text{PP})$ value at -70°C of 50 Hz is typical of tetrahedral platinum(0) phosphine complexes [25]. The $J(\text{PtP})$ values for the triphenylphosphine ligands in $\text{Pt}(\text{PPh}_3)_2(\text{SP})$ (4009, 4035 Hz) fall between the values for tetrahedral $\text{Pt}(\text{PPh}_3)_4$ (3829 Hz) [16] and trigonal $\text{Pt}(\text{PPh}_3)_3$ (4438 Hz [16], 4370 Hz [11]). Thus the abnormally low $J(\text{PtP})$ value for bidentate SP in $\text{Pt}(\text{PPh}_3)_2(\text{SP})$ probably indicates that its Pt–P bond has less *s*-character than the Pt–P bond in a normal tetrahedral complex; this could occur because the P–Pt–olefin ‘bite’ angle is only 90 – 100° [18], i.e. ca. 10 – 20° less than the normal tetrahedral angle. The remaining Pt–P bonds to the triphenylphosphine ligands will be rehybridized to include more *s*-character and

will, therefore, exhibit larger values of $J(\text{PtP})$ than in $\text{Pt}(\text{PPh}_3)_4$. A similar argument has been advanced to account for the trends in $J(\text{PtP})$ in the series $\text{Pt}(\text{triphos})\text{L}$ (triphos = $\text{MeC}(\text{CH}_2\text{PPh}_2)_3$; $\text{L} = \text{PPh}_3$, $\text{P}(\text{C}_6\text{H}_4\text{Me-}p)_3$, PMePh_2 , $\text{P}(\text{OCH}_2)_3\text{CMe}$, PF_2NMe_2 , PF_3), where the geometric constraint of the tripodal ligand gives remarkably small values of $J(\text{PtP})$ for the $\text{Pt-P}(\text{triphos})$ bonds and correspondingly larger than normal values of $J(\text{PtP})$ for the remaining Pt-P bond [26].

The structure of the palladium(0) complex $\text{Pd}(\text{PPh}_3)_2(\text{SP})$ is unknown because it disproportionates immediately on dissolution giving $\text{Pd}(\text{PPh}_3)(\text{SP})_2$ and $\text{Pd}(\text{PPh}_3)_3$. The platinum(0) and nickel(0) complexes disproportionate more slowly in solution to give $\text{M}(\text{SP})_2$, $\text{M}(\text{PPh}_3)_3$ and PPh_3 ($\text{M} = \text{Pt}, \text{Ni}$). This difference in behaviour may reflect the lower affinity for olefins of Pd^0 relative to Pt^0 and Ni^0 , as indicated also by the structures of the $\text{M}(\text{SP})_2$ complexes (see Introduction). The rapid disproportionation of platinum(0) complexes containing different tertiary phosphines is well known and relatively few compounds of this type have been isolated [26–29]; analogous nickel(0) and palladium(0) complexes are apparently unknown.

Both $\text{Ni}(\text{PPh}_3)_2(\text{SP})$ and $\text{Pt}(\text{PPh}_3)_2(\text{SP})$ undergo ready intermolecular exchange of coordinated PPh_3 at low temperature, but the platinum compound differs from the nickel compound in that it also undergoes a low-energy intramolecular process involving the coordinated vinyl group of SP ; this equivalences the triphenylphosphine ligands before the onset of intermolecular exchange. The fact that only the platinum compound shows this behaviour suggests that the process is not chelate ring inversion, which might be expected to occur with approximately equal facility for both compounds, but one-ended dissociation of the vinyl group. If this is correct, the implication is that $\text{Pt}(\text{PPh}_3)_2(\text{SP})$ prefers to lose its coordinated olefin whereas $\text{Ni}(\text{PPh}_3)_2(\text{SP})$ prefers to lose PPh_3 , a trend which is in line with the relative affinities of the fragments $\text{M}(\text{PPh}_3)_2$ ($\text{M} = \text{Pt}, \text{Ni}$) for ethylene and triphenylphosphine expressed by the equilibrium constants for eq. 1 [11].

Experimental

All reactions were carried out under dry nitrogen or argon using standard Schlenk techniques. All solvents used were of analytical grade. Toluene was distilled from sodium benzophenone ketyl under nitrogen. Hexane was dried over sodium wire and was degassed before use. Deuterated solvents were degassed by freeze/thaw cycles. Microanalyses and osmometric molecular weight measurements (Knauer vapour pressure osmometer) were carried out by the Research School of Chemistry Micro-analytical Service (Miss Brenda Stevenson and associates).

Phosphorus-31 NMR spectra were recorded either on a Bruker B-KR322S spectrometer at 24.28 MHz or on a Bruker CXP200 spectrometer at 80.98 MHz. Chemical shifts are reported in ppm to high frequency of external 85% H_3PO_4 . Proton NMR spectra were measured on Bruker CXP200 or JEOL FX200 spectrometers at 200 MHz. Chemical shifts are reported in ppm to high frequency of internal tetramethylsilane. Infrared spectra were recorded as KBr disks on a Perkin–Elmer 683 instrument. The compounds $\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$ [30], $\text{Pd}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$ [31], $\text{Ni}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$ [10], $\text{Pt}(1,5\text{-COD})_2$ [32], $\text{Ni}(1,5\text{-COD})_2$ [33], (2-vinylphenyl)-diphenylphosphine (SP) [34] and 1,2-bis(dicyclohexylphosphino)ethane, $\text{Cy}_2\text{PCH}_2\text{-CH}_2\text{PCy}_2$ [35] were prepared by literature methods; the preparation of $\text{Pt}(\text{Cy}_2\text{PCH}_2\text{CH}_2\text{PCy}_2)(\text{C}_2\text{H}_4)$ will be reported elsewhere [36].

Preparations

(1) *Bis(triphenylphosphine){(2-vinylphenyl)diphenylphosphine} platinum(0)*, $Pt(PPh_3)_2(SP)$. (a) Solid $Pt(PPh_3)_2(C_2H_4)$ (0.83 g, 1.11 mmol) was added to a solution of SP (0.32 g, 1.11 mmol) in toluene (100 ml) at room temperature. The initially colourless solution turned yellow and gas was evolved immediately. The solution was stirred at room temperature for 30 min and evaporated to ca. 40 ml under reduced pressure. On addition of hexane, a bright yellow crystalline solid precipitated. The mixture was cooled in a dry-ice/acetone bath and the solid was filtered off, washed with hexane (3×25 ml), and dried in vacuo for 3 h to give $Pt(PPh_3)_2(SP)$ (0.85 g, 82%). Anal. Found: C, 66.6; H, 4.7; P, 9.5; mol. wt (toluene, $37^\circ C$) 491. $C_{56}H_{47}P_3Pt$ calcd.: C, 66.7; H, 4.7; P, 9.2%; mol. wt, 1008.

(b) A solution of $Pt(1,5-COD)_2$ (0.05 g, 0.12 mmol) in toluene (10 ml) was added to a solution containing SP (0.035 g, 0.12 mmol) and triphenylphosphine (0.064 g, 0.24 mmol) in toluene (10 ml). The initially colourless solution turned yellow immediately. After being stirred at room temperature for 30 min, the solution was evaporated to dryness and the residue was dried in vacuo for 3 h. Recrystallization from toluene/hexane gave a yellow crystalline solid which was washed with hexane (3×20 ml) and dried in vacuo for 3 h to give $Pt(PPh_3)_2(SP)$ (0.1 g, 85%), identified by 1H and ^{31}P NMR spectroscopy.

(2) *Bis(triphenylphosphine){(2-vinylphenyl)diphenylphosphine} palladium(0)*, $Pd(PPh_3)_2(SP)$. A solution of $Pd(PPh_3)_2(C_2H_4)$ (4.0 g, 6.17 mmol) in toluene (100 ml) was cooled in a dry-ice/acetone bath and was added to a similarly cooled solution of SP (1.75 g, 6.17 mmol) in toluene (100 ml). The initially colourless solution turned yellow and gas was evolved. The mixture was stirred at $-70^\circ C$ for 30 min and evaporated to approximately half-volume in vacuo. Addition of hexane precipitated a pale yellow solid which was filtered off at $-70^\circ C$, washed with cold hexane (3×50 ml) and dried in vacuo to give $Pd(PPh_3)_2(SP)$ (3.7 g, 65%). The solid gradually darkened when it was stored at room temperature. Anal. Found: C, 72.0; H, 5.3; P, 10.0; mol. wt (toluene, $37^\circ C$), 503. $C_{56}H_{47}P_3Pd$ calcd.: C, 73.2; H, 5.15; P, 10.1%; mol. wt, 919.

(3) *Attempted isolation of Bis(triphenylphosphine){(2-vinylphenyl)diphenylphosphine} nickel(0)*, $Ni(PPh_3)_2(SP)$. (a) A solution of $Ni(PPh_3)_2(C_2H_4)$ (5.0 g, 8.18 mmol) in toluene (30 ml) was added to a solution of SP (2.35 g, 8.18 mmol) in toluene (30 ml). There was an immediate colour change from yellow to orange-red and gas was evolved. The mixture was stirred at room temperature for 30 min and the volume reduced to about half under reduced pressure. The solution was cooled in a dry-ice/acetone bath and hexane was added to precipitate an orange solid. This was filtered off, washed with hexane (3×20 ml), and dried in vacuo to give 6.1 g of product. Anal. Found: C, 72.0; H, 5.35; P, 10.1; Ni, 6.9. $C_{56}H_{47}P_3Ni$ calcd.: C, 77.2; H, 5.4; P, 10.7; Ni, 6.7%. The 1H and ^{31}P NMR spectra showed the product to be a mixture of $Ni(PPh_3)_2(SP)$, $Ni(SP)_2$, $Ni(PPh_3)_n$ ($n = 3, 4$) and $o-CH_2=CHC_6H_4P(O)Ph_2$ (see text).

(b) A solution of $Ni(1,5-COD)_2$ (0.45 g, 1.45 mmol) in toluene (40 ml) was added to a solution containing triphenylphosphine (0.76 g, 2.90 mmol) and SP (0.42 g, 1.45 mmol) in toluene (40 ml). The resulting orange-red solution was stirred for 30 min and evaporated to dryness in vacuo. After being dried in vacuo for 3 h, the orange solid was recrystallized from toluene/hexane. The solid was filtered off, washed with hexane (3×20 ml), and dried in vacuo to give 1.0 g of product. The 1H and ^{31}P

NMR spectra were similar to those of the solid prepared above.

(4) *Attempted preparation of Pt(dppe)(SP)*. A solution of Pt(1,5-COD)_2 (0.073 g, 0.18 mmol) in toluene was added to a solution containing dppe (0.071 g, 0.18 mmol) and SP (0.051 g, 0.18 mmol) in toluene (20 ml). The yellow reaction mixture was stirred for 30 min and n-pentane was added to give a yellow precipitate. The product was filtered off, washed with ether (3×20 ml), and dried in vacuo for 3 h. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum in toluene showed peaks at δ 31.4 ($^1\text{J}(\text{PtP})$ 3795 Hz) and δ 17.5 ($^1\text{J}(\text{PtP})$ 3130 Hz) in a 1/1 ratio due to Pt(dppe)_2 and Pt(SP)_2 , respectively. These were also observed in a solution prepared in situ from Pt(1,5-COD)_2 , dppe and SP in a 1/1/1 ratio.

(5) *Attempted preparation of Pt(Cy₂PCH₂CH₂PCy₂)(SP)*. Benzene (30 ml) was added to a solid mixture of $\text{Pt(Cy}_2\text{PCH}_2\text{CH}_2\text{PCy}_2\text{)(C}_2\text{H}_4\text{)}$ (0.088 g, 0.14 mmol) and SP (0.058 g, 0.20 mmol). The pale yellow solution was stirred at room temperature for 3 h. Evaporation to ca. half-volume and addition of n-pentane gave an off-white solid which was washed with n-pentane (3×10 ml) and dried in vacuo. This was shown by ^1H and ^{31}P NMR spectroscopy to contain predominantly starting compound together with a small amount of unidentified material.

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