RESEARCH ARTICLE
DOI: https://doi.org/10.4038/ouslj.v20i1.7703

OUSL Journal, 2025
Vol. 20, No. 1, (pp. 115-126)

Mo and Pt Complexes of an Azine Phosphine with a Ferrocene Moiety

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Abstract

Condensation of the phosphino hydrazone *Z*-$PPh_2CH_2C(Bu^t)=NNH_2$ **II** with ferrocene carboxaldehyde, $CpFe(C_5H_4CHO)$ produced the azine monophosphine *Z,E*-$PPh_2CH_2C(Bu^t)=N\text{-}N=CH(C_5H_4)FeCp$ (*Z,E*-**LH**). The reaction of *Z,E*-**LH** with the labile $[Mo(CO)_4(nbd)]$ (nbd = norbornadiene) at room temperature afforded the orange tetracarbonyl Mo(0) complex $[Mo(CO)_4(Z,E\text{-LH})]$ (**3**), *Z,E*-**LH** is a bidentate ligand. When (**3**) was heated in boiling toluene, isomerization around the $-N=CH(C_5H_4)FeCp$ double bond occurred, and the resulting red complex $[Mo(CO)_4(Z,Z\text{-LH})]$ (**4**) was isolated in 78% yield. Treatment of $[PtMe_2(cod)]$ (cod = cycloocta-1,5-diene) with the ligand *Z,E*-**LH** at 20 °C formed the dimethylplatinum(II) complex $[PtMe_2(Z,E\text{-LH})]$ (**5**) in which the H^2-proton attached to the cyclopentadienyl group showed agostic interaction with the platinum(II) centre. When the complex (**5**) was heated in boiling

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(Received 26th October 2024; Revised 14th June 2025; Accepted 30th June 2025)

toluene, the C-H(agostic) bond underwent an oxidative activation reaction followed by a loss of methane molecule to give the cyclometallated platinum(ll) complex [PtMe(*Z,E*-L)] (**6**), with the tridentate P^N^C ligand. The compounds were adequately characterized using IR, NMR, mass spectrometry, and elemental analysis.

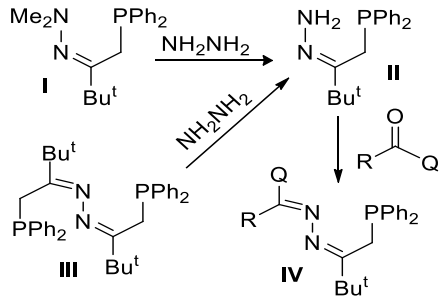
Keywords: *Mo(0)/Pt(II) complexes, ferrocene, azine phosphine, cyclometallation, agostic interaction*

Introduction

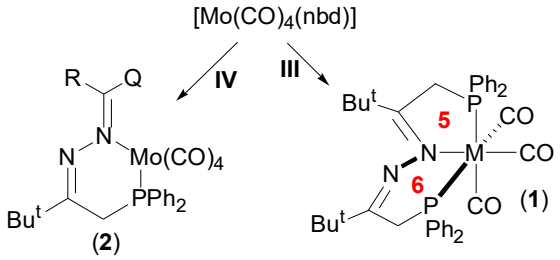
Shaw and coworkers reported the synthesis of the phosphino dimethyl hydrazone **I** and phosphino hydrazone *Z*-$PPh_2CH_2C(Bu^t)=NNH_2$ **II** (Scheme 1) (Hii et al., 1992). The Ligand **II** was also prepared by reacting the azine diphosphine, *Z,Z*-$PPh_2CH_2C(Bu^t)=N-N=C(Bu^t)CH_2PPh_2$ **III** (Perera et al., 1992) with an excess of hydrazine hydrate (Hii et al., 1992). The Ligand **II** condenses readily with aldehydes or ketones, R(C=O)Q (where R and Q are organic groups; R is smaller than Q) to give the azine monophosphine *Z,E*-$PPh_2CH_2C(Bu^t)=N-N=CR(Q)$ **IV** (Hii et al., 1992; Hii et al., 1994; Perera & Shaw, 1994a & 1994b; Perera et al., 1998). The coordination chemistry of azine monophosphines with Group 6 metal carbonyls (Hii et al., 1992; Perera et al., 1998), palladium (Hii et al., 1994), platinum (Hii et al., 1994; Perera et al., 1998), ruthenium (Perera & Shaw,1994a; Perera et al., 1998) and iridium (Perera & Shaw,1994b; Perera et al., 1995; Perera et al., 1998) was reported.

An azine such as **III** can have three isomers, (*e.g.*, *Z,Z-*, *Z,E-* and *E,E-*). The energy barrier to rotation around the C=N bond is relatively low, and interconversions can be achieved thermally. In the presence of a metal centre, the isomerization around the C=N bond in phosphino dimethylhydrazone **I**, azine diphosphine **III** and azine monophosphine **IV** was reported (Hii et al., 1992; Perera et al., 1992; Perera et al., 1998; Hii et al., 1994; Ike et al., 1998). At low temperatures, the molybdenum complex with the *Z,E*-isomer was formed (Scheme 2) (Perera et al., 1992; Perera et al., 1998).

The x-ray crystal structures of *fac*-[$Mo(CO)_3$(*Z,E*-**III**)] (**1**) (Perera et al., 1992) [$Mo(CO)_4${*Z,E*-$PPh_2CH_2C(Bu^t)$=NN=$CMe(C_6H_4NO_2$-4)] (**2**) (Perera et al., 1998) were determined.



Scheme 1. Synthetic routes to ligands **II**, **III**, and **IV**



Scheme 2. Mo complexes of **III** and **IV**

In the ^{13}C NMR spectra of complexes (**1**) (Perera et al., 1992) and (**2**) (Perera et al., 1998), the CH_2 carbon in the six-membered ring appeared as a doublet at δ_C 25.5 ppm whilst in the complex (**1**), the CH_2 carbon in the five-membered ring appeared as a doublet at δ_C 44.8 ppm (Perera et al., 1992). Similar NMR studies on Pd, Pt and Ir complexes of azine monophosphine have shown lower δ_C values (between 20-25 ppm) for methylene carbons in six-membered rings and higher δ_C values (between 40-45 ppm) for methylene carbons in five-membered rings (Perera et al., 1992; Perera et al., 1998; Ike et al., 1998; Ike et al., 1995).

Since the ferrocenyl group is a stable organometallic group with

interesting electrochemical properties, it was decided to study the coordination chemistry of a ferrocene-based azine phosphine ligand. In this paper, the synthesis of the ferrocene-based azine monophosphine *Z,E*-$PPh_2CH_2C(Bu^t)$=N-N=$CH(C_5H_4)FeCp$ (*Z,E*-**LH**) and its complexes with molybdenum and platinum centres are presented.

Methodology

All the reactions were carried out in an inert atmosphere of dry nitrogen. NMR spectra were recorded using a JEOL FX-100 spectrometer (operating frequencies for ^1H and ^{31}P of 99.5 and 40.25 MHz, respectively), and a Bruker ARX-250 (operating frequencies for ^1H, ^{31}P and ^{13}C were 400.13, 161.9 and 100.6 MHz, respectively). ^1H and ^{13}C chemical shifts are in ppm relative to tetramethyl silane and ^{31}P shifts are relative to 85% phosphoric acid. Coupling constants are in Hz. Infrared spectra were recorded using a Perkin Elmer model 257 grating spectrometer (4000-600 cm^{-1}) or a Pye Unicam SP2000 (4000-200 cm^{-1}). Fast atom bombardment (FAB) mass spectra were recorded using VG Autospec spectrometer using with an 8kV acceleration.

***Z,E*-$PPh_2CH_2C(Bu^t)$=N-N=$CH(C_5H_4)FeCp$** (*Z,E*-**LH**)

The ligand *Z,E*-**LH** was prepared by condensing the phosphine *Z*-$PPh_2CH_2C(Bu^t)$=NNH_2 with ferrocene carboxaldehyde $CpFe(C_5H_4CHO)$ according to a literature procedure (Hii et al., 1992). Yield 86%, (Found: C, 70.15; H, 6.25; N, 5.8. $C_{29}H_{31}N_2PFe$ requires C, 70.45; H, 6.32; N, 5.65%). Mass (EI): *m/z* 494 (M^+) and 437 (M-Bu^t). IR (KBr): ν(C=N) = 1625 cm^{-1}. ^{31}P-{^1H} NMR (101 MHz, $CDCl_3$), δ_P (ppm): –8.2. ^1H NMR (250 MHz, $CDCl_3$, δ_H (ppm): 1.11 (9H, s, Bu^t), 3.43 (2H, d, $^2J(PH)$ = 3.9, CH_2P), 4.15 (5H, s, C_P), 4.32 (2H, m, $H^{2,5}$ or $H^{3,4}$). 4.42 (2H, m, $H^{2,5}$ or $H^{3,4}$) and 8.09 (1H, s, HC=).

[Mo(CO)$_4$(*Z,E*-LH)] (3)

A solution containing the azine phosphine *Z,E*-**LH** (150 mg 0.3 mmol) and [Mo(CO)$_4$(nbd)] (104 mg, 0.35 mmol) in benzene (3 mL) was put aside at *ca.* 20 °C for 1.5 h. The solvent was then removed to a smaller volume under reduced pressure to give (**3**) as orange microcrystals. These were filtered off, washed with cold methanol, and dried *in vacuo* (yield 150 mg, 71%). (Found: C, 56.3; H, 4.3; N, 3.9 $C_{33}H_{31}FeMoN_2O_4P$ requires C, 56.4; H, 4.45; N, 4.0%). IR (KBr, cm^{-1}): ν(C=N) = 1595 cm^{-1}. IR (dichloromethane, cm^{-1}): ν(C≡O) = 2010s, 1880s and 1840s. Mass (FAB): *m/z* 704 (M$^+$), 648 (M-2CO) and 592 (M-4CO). ^{31}P-{^{1}H}-NMR (101 MHz, $CDCl_3$), δ_P (ppm): 47.8(s). ^{1}H NMR (250 MHz, $CDCl_3$) δ_H (ppm): 0.85 (9H, s, Bu^t), 2.70 (1H, t, ^{2}J(PH) = ^{3}J(HH) 12.2), 3.32 (1H, t, ^{2}J(PH) = ^{3}J(HH) 12.2), 4.34 (5H, s, C_P), 4.56 (2H, m, $H^{2,5}$ or $H^{3,4}$), 5.51 (2H, m, $H^{2,5}$ or $H^{3,4}$) and 7.84 (1H, d, ^{4}J(PH) 1.9, HC=). ^{13}C-{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ_C 24.8 [1C, d, ^{1}J(PC) 6.8, CH_2], 27.4 (3C, s, C*Me$_3$*), 38.6 [1C, d, ^{3}J(PC) 1.8, CMe_3], 69.6 (7C, s, $C^{2,5}$ or $C^{3,4}$ and C_P), 71.8 (2C, s, $C^{2,5}$ or $C^{3,4}$), 75.9 (1C, s, C^1), 160.9 [1C, d, ^{3}J(PC) 4.1, HC=N], 170.9 (1C, s, Bu^{t}C=N), 208.2 [2C, d, ^{2}J(PC) 8.6, C≡O, mutually *trans*], 215.9 [1C, d, ^{2}J(PC) 35.9, C≡O, *trans* to P] and 219.9 [1C, d, ^{2}*J*(PC) 6.9, C≡O, *trans* to N].

[Mo(CO)$_4${*Z,Z*-LH)] (4)

A solution of the tetracarbonylmolybdenum(0) complex (**3**) (80 mg, 0.11 mmol) in toluene (2 mL) was heated at *ca.* 100 °C for 75 min. The reaction mixture was cooled to *ca.* 20 °C, the solvent removed under reduced pressure and the residue triturated with methanol to give (**4**) as a red solid. This was filtered off, washed with cold methanol, and dried *in vacuo* (yield 62 mg, 78%). (Found: C, 56.6; H, 4.1; N, 3.85 $C_{33}H_{31}FeMoN_2O_4P$ requires C, 56.4; H, 4.45; N, 4.0%). IR (KBr, cm^{-1}): ν(C=N) = 1600m. IR (dichloromethane, cm^{-1}): ν(C≡O) = 2025s, 1905s and 1850s. Mass (FAB): *m/z* 704 (M$^+$), 648 (M-2CO), 620 (M-3CO) and 592 (M-4CO). ^{31}P-{^{1}H}-NMR (101 MHz, $CDCl_3$), δ_P (ppm): 50.3(s). ^{1}H NMR (250 MHz, $CDCl_3$) δ_H (ppm):

0.87 (9H, s, Bu^t), 2.51 (1H, t, $^2J(PH) = {}^3J(HH)$ 11.7, CH_2P), 3.45 (1H, m, $^2J(PH)$ 17.7, $^3J(HH)$ 11.7, CH_2P), 4.22 (5H, s, Cp), 4.42 (2H, m, $H^{2,5}$ or $H^{3,4}$), 4.54 (2H, m, $H^{2,5}$ or $H^{3,4}$) and 7.80 (1H, d, $^4J(PH)$ 1.0, HC=). $^{13}C-\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ_C 25.3 [1C, d, $^1J(PC)$ 7.1, CH_2], 27.3 (3C, s, C*Me*$_3$), 38.8 [1C, d, $^3J(PC)$ 1.8, *C*Me_3], 69.8 (5C, s, C_P), 69.8 (2C, s, $C^{2,5}$ or $C^{3,4}$), 72.4 (2C, s, $C^{2,5}$ or $C^{3,4}$), 73.6 (1C, s, C^1), 159.0 [1C, d, $^3J(PC)$ 4.1, HC=N], 169.4 (1C, s, Bu^tC=N), 208.2 [1C, d, $^2J(PC)$ 9.2, 2C≡O, mutually *trans*], 216.1 [1C, d, $^2J(PC)$ 36.4, C≡O, *trans* to P] and 220.3 [1C, d, $^2J(PC)$ 6.7, C≡O, *trans* to N].

[$PtMe_2$(*Z,E*-LH)] (5)

A solution of the azine phosphine *Z,E*-**LH** (150 mg 0.3 mmol) and [$PtMe_2$(cod)] (101 mg, 0.3 mmol) in benzene (2 mL) was put aside at *ca.* 20 °C for 1.5 h. The dimethylplatinum(II) complex **(5)** crystallized out from the resultant orange solution as orange microcrystals. Yield (162 mg, 75%). (Found: C, 51.45; H, 4.9; N, 3.75. $C_{31}H_{37}N_2PFePt$ requires C, 51.75; H, 5.2; N, 3.9%). Mass (FAB): m/*z* 719 (M^+), 704 (M-Me) and 688 (M-Me-CH_4). IR (KBr): ν(C=N) = 1610 cm^{-1}. $^{31}P-\{^1H\}$ NMR (101 MHz, $CDCl_3$), δ_P (ppm): 31.1(s), $^1J(PtP)$ = 2133 Hz. ^1H NMR (250 MHz, $CDCl_3$) δ_H (ppm): 0.44 [3H, d, $^3J(PH)$ 8.0, $^2J(PtH)$ 69.8, PtMe], 0.79 [3H, d, $^3J(PH)$ 7.5, $^2J(PtH)$ 88.5, PtMe], 0.89 (9H, s, Bu^t), 2.48 [1H, dd, $^2J(PH)$ 11.4, $^2J(HH)$ 12.6, $^3J(PtH)$ 8.2, CH_2P], 3.55 [1H, dd, $^2J(PH)$ 10.5, $^2J(HH)$ 12.6, $^3J(PtH)$ 19.4, CH_2P], 3.79 (5H, s, C_P), 4.38 (1H, dt, $^3J(HH)$ 2.6, $^4J(HH)$ 1.3, H^4), 4.44 (1H, m, H^3), 4.51 (1H, dt, $^3J(HH)$ 2.6, $^4J(HH)$ 1.3, H^5), 6.18 (1H, m, $^3J(HH)$ 2.6, $^4J(HH)$ 1.3, 0.6, $^1J(PtH)$ ~ 10, H^2) and 8.26 [1H, d, $^4J(PH)$ 1.7, $^3J(PtH)$ 39.7, HC=]. $^{13}C-\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ_C -22.7[1C, d, $^2J(PC)$ 3.7, $^1J(PtC)$ 746, PtMe *trans* to N], -8.5 [1C, d, $^2J(PC)$ 111, $^1J(PtC)$ 667, PtMe *trans* to P], 24.5 [1C, d, $^1J(PC)$ 18.2, CH_2], 27.5 (3C, s, C*Me*$_3$), 38.9 [1C, d, $^3J(PC)$ 2.0, *C*Me_3], 68.9 (5C, s, C_P), 69.6 (1C, s, $C^{2,3,4\text{ or }5}$), 71.3 (1C, s, $C^{2,3,4,\text{ or }5}$), 71.8 (1C, s, $C^{2,3,4,\text{ or }5}$), 72.7 (1C, s, $C^{2,3,4\text{ or }5}$), 75.4 (1C, s, C^1), 128.3 [2C, d, $^3J(PC)$ 9.9, C_{meta}], 128.8 [2C, d, $^3J(PC)$ 9.1, C_{meta}], 130.2 (1C, s, C_{para}), 130.6 (1C, s, C_{para}) 131.8 [1C, d, $^1J(PC)$ 34.8, $^2J(PtC)$ 21.5, C_{ipso}], 132.3 [2C, d, $^2J(PC)$ 12.3, $^3J(PtC)$ 16.4,

C_{ortho}], 133.9 [1C, d, ^{1}J(PC) 35.5, ^{2}J(PtC) 22.9, C_{ipso}], 134.6 [2C, d, ^{2}J(PC) 13.5, ^{3}J(PtC) 25.0, C_{ortho}], 154.4 [1C, d, J(PC) 3.2, C=N] and 172.6 [1C, s, J(PtC) 19.8, C=N].

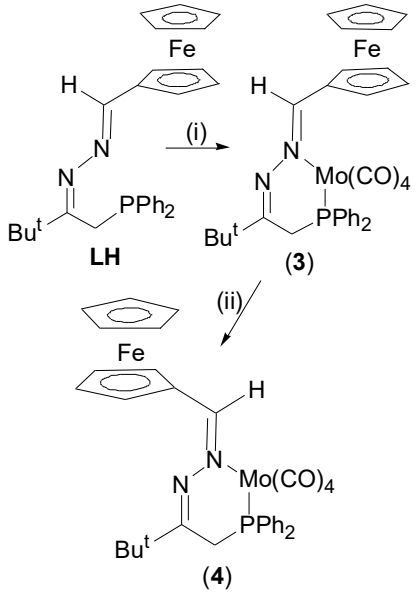
[PtMe(*Z,E*-L)] (6)

A suspension of the dimethylplatinum(II) complex (**5**) (103 mg, 0.14 mmol) in toluene (2 mL) was heated at *ca.* 110 °C for 40 h. The resultant purple solution was cooled to *ca.* 20 °C, evaporated to a low volume under reduced pressure and the residue triturated with methanol to give (**6**) as a purple solid. This was filtered off, washed with cold methanol and dried in vacuo. Yield (69 mg, 70%). (Found: C, 52.4; H, 4.9; N, 3.8. $C_{30}H_{33}N_2PFePt{\cdot}0.25C_6H_5CH_3$ requires C, 52.5; H, 4.9; N, 3.85%). Mass (FAB): m/z 688 (M-Me). IR (KBr): ν(C=N) = 1610 cm^{-1}. ^{31}P-{^{1}H}-NMR (101 MHz, C_6D_6), δ_P (ppm): 26.1(s), ^{1}J(PtP) = 2439 Hz. ^{1}H NMR (100 MHz, C_6D_6), δ_H (ppm) : 0.85 (9H, s, Bu^t), 1.70 [3H, d, ^{3}J(PH) 7.3, ^{2}J(PtH) 90.0, PtMe], 2.85 [1H, dd, ^{2}J(PH) 10.8, ^{2}J(HH) 13.3, ^{3}J(PtH) 18.4, CH_2P], 3.23 [1H, t, ^{2}J(PH) = ^{2}J(HH) 13.3, ^{3}J(PtH) 23.0, CH_2P], 4.33 (5H, s, C_P), 4.61 (1H, m, H^3 ,H^4 or H^5), 4.68 (1H, m, H^3, H^4 or H^5), 5.14 (1H, m, H^3, H^4 or H^5) and 9.05 [1H, s, ^{3}J(PtH) 31.0, HC=N]. ^{13}C-{^{1}H}NMR (100.6 MHz, C_6D_6): δ_C –23.9 [1C, d, ^{2}J(PC) 5.1, ^{1}J(PtC) 728, PtMe], 22.9 [1C, d, ^{1}J(PC) 23.6, CH_2], 27.7 (3C, s, C*Me*$_3$), 40.5 [1C, d, ^{3}J(PC) 2.6, *C*Me$_3$], 69.3[1C, d, ^{4}J(PC) 4.7, ^{3}J(PtC) 32.0, C^4 or C^5], 69.8 (5C, s, C_P), 74.7 [1C, d, ^{4}J(PC) 7.7, ^{3}J(PtC) 57.3, C^4 or C^5], 76.3 [1C, d, ^{3}J(PC) 7.9, ^{2}J(PtC) 134.2, C^3], 87.5 [1C, d, ^{3}J(PC) 4.8, C^1], 106.5 [1C, d, ^{2}J(PC) 135.0, ^{1}J(PtC) 502, C^2], 128.4 [2C, d, ^{3}J(PC) 8.0, C_{meta}], 128.5 [2C, d, ^{3}J(PC) 9.9, C_{meta}], 129.9 (1C, s, C_{para}), 130.8 (1C, s, C_{para}), 132.4 [1C, d, ^{1}J(PC) 48.3, C_{ipso}], 132.6 [2C, d, ^{2}J(PC) 10.9, ^{3}J(PtC) 14.6, C_{ortho}], 132.7 [1C, d, ^{1}J(PC) 39.2, C_{ipso}], 134.7 [2C, d, ^{2}J(PC) 13.1, ^{3}J(PtC) 24.0, C_{ortho}], 167.3 (1C, s, C=N) and 175.7 [1C, d, ^{3}J(PC) 2.8, J(PtC) 44.7, C=N].

Results and Discussion

Condensation of *Z*-$PPh_2CH_2C(Bu^t)=NNH_2$ **II** with the carboxaldehyde $CpFe(C_5H_4CHO)$ (Scheme 3) afforded the *Z,E*-azine monophosphine, *Z,E*-$PPh_2CH_2C(Bu^t)=N\text{-}N=CH(C_5H_4)FeCp$ (*Z,E*-**LH**).

The ligand *Z,E*-**LH** and other metal complexes were adequately characterized using IR, NMR, mass spectrometry and elemental analysis. The ^{1}H NMR spectrum showed three singlets at 1.11 (9H), 4.15 (5H), and 8.09 (1H) ppm for the Bu^{t}, Cp, and HC=N groups, respectively. The phosphorus-31 resonance was a singlet at -8.3 ppm.



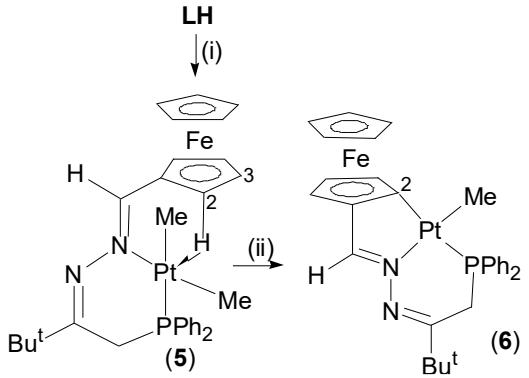
Scheme 3. Mo complexes of *Z,E*-**LH**; (i) [Mo(CO)$_4$(nbd)]; (ii) heat

First, the coordination chemistry of this ligand was studied with zerovalent molybdenum centres stabilised by carbonyl ligands (Scheme 3). The reaction of *Z,E*-**LH** with labile [Mo(CO)$_4$(nbd)] (nbd = norbornadiene) at *ca.* 20^{o}C for 1.5 h resulted in the formation of orange tetracarbonylmolybdenum(0) complex [Mo(CO)$_4$(*Z,E*-LH)}] (**3**) with a six-membered chelate based-on NMR data. NMR data were assigned using ^{13}C-^{1}H-COSY experiments. In the ^{13}C NMR spectrum, the doublet at 24.8 {^{1}J(PC) = 6.8 Hz} was assigned to the CH_2 carbon in the six-membered ring, and the four carbonyl ligands appeared as three doublets at 208.2, 215.9 and 219.9 ppm in the intensity ratio of 2:1:1. The signal at 208.2 ppm was assigned to the two axial carbonyl ligands. The IR spectrum of (**3**)

showed three IR bands at 2010, 1880 and 1840 cm^{-1} for the carbonyl ligands. These values are in good agreement with the literature values (Hii et al., 1992; Perera et al., 1998). The phosphorus-31 resonance was a singlet at 47.8 ppm.

When the complex (**3**) was heated in toluene at ca. 110 °C for 75 min, isomerization around HC=N double bond took place to produce a red Mo(0) complex [$Mo(CO)_4$(*Z,Z*-LH)] (**4**) in 78% yield. The phosphorus-31 resonance was a singlet at 50.3 ppm and the carbon resonances for the four carbonyl ligands appeared at 208.2, 216.1 and 220.3 ppm with the intensity ratio of (2:1:1). The doublet at δ_C 25.3 with $^1J(PC)$ = 7.1 Hz for the CH_2 carbon confirmed the presence of a six-membered chelate ring.

Reaction of [$PtMe_2$(cod)] (cod = cycloocta-1,5-diene) with the ligand *Z,E*-**LH** (Scheme 4) at 20 °C gave the dimethylplatinum(II) complex [$PtMe_2$(*Z,E*-LH)] (**5**).



Scheme 4. Platinum(II) complexes of *Z,E*-**LH**; (i) [$PtMe_2$(cod)]; (ii) heat

Elemental analysis and mass spectral data are in good agreement with the composition of (**5**). The ^{31}P NMR spectrum showed a singlet at δ_P 31.1 ppm with platinum-195 satellites, $^1J(PtP)$ = 2133 Hz, indicating that phosphorus is *trans* to a methyl group. In the ^{13}C NMR spectrum, two doublets at δ_C -22.7 ppm with {$^2J(PC)$ = 3.7 Hz, $^1J(PtC)$ = 746 Hz} and -8.5 ppm with [$^2J(PC)$ = 111 Hz, $^1J(PtC)$ = 667 Hz} were assigned to methyl groups *trans* to nitrogen and

phosphorus, respectively. In the ^{1}H NMR spectrum, the H^{2}-proton attached to the cyclopentadienyl group showed a multiplet with Pt-195 satellites ($^{1}J(PtH)$ ~ 10 Hz) at 6.18 ppm due to agostic interaction with the platinum(II) centre. Azine monophosphine ligands have been used to promote agostic interactions with ruthenium(II) centres (Perera & Shaw, 1994a; Perera & Shaw, 1995a; Perera et al., 1998).

When (**5**) was heated in boiling toluene, the C-H bond with the agostic proton underwent oxidative addition reaction to form the Pt(IV) intermediate [$PtHMe_2$(*Z,E*-L)], which reductive eliminated a methane molecule to produce the cyclometallated methylplatinum(ll) complex [PtMe(*Z,E*-L)] (**6**) where L is an anionic tridentate P^N^C ligand. The characterizing data are in good agreement with the proposed structure. In the ^{13}C NMR spectrum, the doublet at δ_C 106.5 ppm with a large coupling to platinum-195 {$^{1}J(PtC)$ = 502 Hz} was assigned to the C^{2} carbon. Cyclometallation *via* a C-H bond activation by Pt(II) (Perera & Shaw,1995b) and Ir(I) centres is well documented (Perera & Shaw, 1994b; Perera et al., 1995; Perera et al., 1998).

Conclusions

The coordination chemistry of a ferrocene-based azine phosphine ligand *Z,E*-**LH** was studied with molybdenum(0) and platinum(II) centres. The tetracarbonyl Mo(0) complex [$Mo(CO)_4$(*Z,E*-LH)] (**3**) was converted into [$Mo(CO)_4$(*Z,Z*-LH)] (**4**) thermally by forcing the isomerization around -N=CH double bond. Interestingly, the Pt(II) complex [$PtMe_2$(*Z,E*-LH)] (**5**) exhibits an agostic interaction between the H^{2}-proton attached to the cyclopentadienyl group and the platinum(II) centre. In boiling toluene, the C-H bond activation of this agostic proton occurred to produce the cyclometallated platinum(II) complex [PtMe(*Z,E*-L)] (**6**) with an anionic tridentate P^N^C ligand.

Acknowledgements

The author wishes to thank the University of Leeds for a Research Fellowship and Late Professor B. L. Shaw for the financial support and laboratory facilities. Author is grateful to Dr. David Shenton for recording some of the NMR spectra.

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