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Syntheses and Characterization of the Complexes of Molybdenum, Tungsten and Palladium with 2-diacetylpyridine-(1*R*)-(-)-fenchone azine

Sintesis dan Pencirian Kompleks Molibdenum, Tungsten dan Paladium dengan 2-asetilpiridina-(1R)-(-)-fencon azin

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Abstract

The diimine 2-diacetylpyridine-(1*R*)-(-)-fenchone azine {fench=NN=CMe}C_5H_5N (4) was prepared by heating 2-diacetylpyridine with fenchone hydrazone (3) in boiling ethanol in the presence of acetic acid as the catalyst. Treatment of $[Mo(CO)_4(nbd)]$, $[Cr(CO)_4(nbd)]$ or $[W(CO)_4(nbd)]$ (nbd = norbornadiene) with 2-diacetylpyridine-(1*R*)-(-)-fenchone azine {fench=NN=CMe}C_5H_5N (4) gave the five-membered chelated N,N bonded carbonyl-complex of (5), (6) or (7), respectively. Treatment of $[PdCl_2(NCPh)_2]$ with the azine ligand (4) gave the palladium-complex (8). Treatment of (8) with LiBr or NaI gave the metathesis product of (9) or (10), respectively. Treatment of $[\{(\eta^3\text{-}2\text{-}MeC_3H_4)PdCl_2\}_2]$ with the azine ligand (4) gave the chloride salt which was then isolated as the corresponding PF_6 salt (11).

Keywords Molybdenum complexes, tungsten complexes, palladium complexes, bidentate N-N ligand complexes, fenchone azine ligand complexes

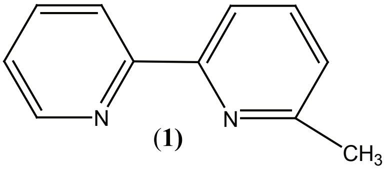
Abstrak

Diimina 2-diasetilpiridina-(1*R*)-(-)-fencon azin {fench=NN=CMe}C_5H_5N (4) telah disediakan dengan memanaskan 2-diasetilpiridina dengan fencon hidrozin (3) dalam etanol yang mendidih dengan kehadiran asid asetik sebagai mangkin. Tindak balas $[Mo(CO)_4(nbd)]$, $[Cr(CO)_4(nbd)]$ atau $[W(CO)_4(nbd)]$ (nbd = norbornadiena) dengan 2-diasetilpiridina-(1*R*)-(-)-fencon azin {fench=NN=CMe}C_5H_5N (4) menghasilkan kompleks-karbonil berkelat N,N ikatan bercincin lima (5), (6) atau (7). Tindak balas $[PdCl_2(NCPh)_2]$ dengan ligan azin (4) menghasilkan kompleks-paladium (8). Tindak balas (8) dengan LiBr atau NaI menghasilkan hasilan metatesis (9) atau (10). Tindak balas $[\{(\eta^3\text{-}2\text{-}MeC_3H_4)PdCl_2\}_2]$ dengan ligan azin (4) menghasilkan garam klorida dan dipisahkan sebagai garam PF_6 (11).

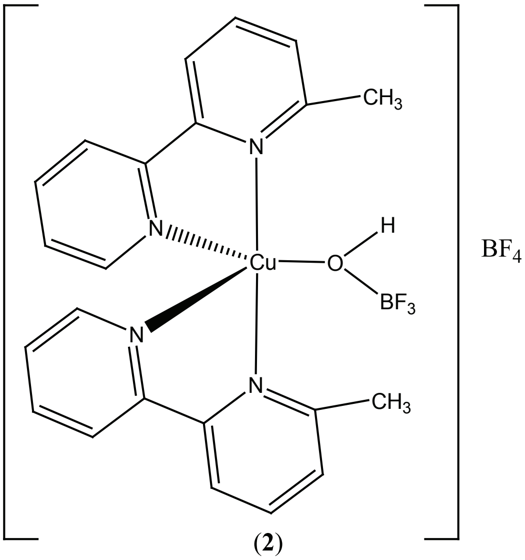
Kata Kunci Kompleks molibdenum, kompleks tungsten, kompleks paladium, kompleks ligan bidentat N-N, kompleks ligan fencon azin

Introduction

Bidentate *N,N*-donor-ligands generated from dimiues have attracted much attention in the past forty years or so due to their versatile coordination behaviour and an interesting properties of their metal complexes (Leonard & Stanley, 1967; Onggo et.al., 1990; Stufkens, 1990; O' Reily, et. al., 2006; Mino et. al., 2006; Raveendran & Pal, 2007; Orsa, et.al., 2008; Muresan, et. al., 2008; Beckford, et. al., 2009 and Volbeda, Meetsma, & Buowkamp, 2009). Additionally, their transition-metal complexes have been used in catalysis (Stufkens, 1990). The complexes of the diimine ligand (1) with copper(II) and palladium(II) have been synthesized and characterized (Onggo et.al., 1990). Treatment of (1) (L) with copper(II) tetrafluoraborate hexahydrate in hot acetone gave the $[CuL_2OHBF_3][BF_4]$, which X-ray crystallography showed to have a structure with essentially a trigonal bipyramidal arrangement around the copper atom (2). Treatment of the (1) with potassium tetrachlopalladate(II) gave the chloropalladium(II) cationic salt which was then isolated as the corresponding BF_4 salt $[PdL_2Cl][BF_4]$ on addition $NaBF_4$ to the reaction mixture. The single crystal X-ray diffraction study showed that the complex (2) has an essentially planar NNNCl environment (Onggo et.al., 1990).



(1)



(2)

In this paper, we report the synthesis of the fenchone derivative (4). Aspects of the coordination chemistry of (4) with group 6 metal carbonyls and palladium(II) are described.

Experimental

All NMR spectra were recorded by using a JEOL FX-90Q spectrometer, a JEOL FX-100 spectrometer, a Brucker ARX-250 or a Bruker AM-400 spectrometer (operating frequencies for ^{1}H and ^{13}C were 400.13 and 100.6 MHz respectively). ^{1}H and ^{13}C chemical shifts are relative to tetramethylsilane and coupling constants are in Hz.

Infrared spectra were recorded by using a Perkin-Elmer model 257 grating spectrometer (4000-600 cm^{-1}) or a Pye Unicam SP2000 (40000-200 cm^{-1}), as Nujol mulls on polyethylene plates, or potassium bromide discs, or as dichloromethane solutions in calcium fluoride cells, with dichloromethane as reference.

Elemental analyses were recorded at the Chemistry Department, University of Leeds UK. As in common with compounds of these types, solvent of crystallisation, particularly CH_2Cl_2 or $CHCl_3$ was often present and could be removed even by prolonged drying. The solvent could be detected in the ^{1}H NMR spectrum.

Electrical conductivities were measured by the using a Phillips PR 9500/01 Conductance and a Standard Conductance cell at 20°C.

Mass spectra were recorded by Mass Spectroscopy Services at University of Leeds, United Kingdom.

(fench=NN=CMe)C_5H_5N (4)

A solution containing (1R)−(-)−fenchone hydrazone (16.75 g, 0.10 mol), 2-diacetylpridine (12.20 g, 0.11 mol) and acetic acid (0.1 cm^3) in ethanol (80 cm^3) was heated at 80°C for 5 h. The reaction mixture was left to stand at ca. 20°C for 1h, after which it was concentrated and cooled at -30°C in which the required product (4) precipitated as a white solid. This was filtered off, washed with cold ethanol and dried. Yield 22.5 mg, 84%. (Found: C, 75.7; H, 8.7; N, 15.7. Calc. for $C_{17}H_{23}N_3$ requires C, 75.8; H, 8.6; N, 15.6%). m/z (EI): 469 (M$^+$). ^{13}C−{^{1}H}NMR (62.9 MHz. $CDCl_3$) δC: 12.8 (1C, s, methyl carbon from fench residue),17.1 (2C, s, methyl carbon from fench residue), 22.2 (1C, s, methyl carbon from fench residue), 51.0 (1C, s, acetyl carbon), 120.6 (1C, s, pyridyl carbon with H), 123.4 (1C, s, pyridyl carbon with H), 135.9 (1C, s, pyridyl carbon with H) and 148.4 (1C, s, pyridyl carbon with H).

[Mo(fench=NN=CMe)C_5H_5N] (5)

A solution containing (4) (1996 mg, 0.74 mmol) and [Mo(CO)$_4$(nbd)] (222 mg, 0.74 mmol) in benzene (5 cm^3) was heated at 80°C for 1 h and left to stand at ca. 20°C for 1h. The solvent was then evaporated to low volume under reduced pressure and methanol added to the residue to give (5) as a reddish brown solid. Yield 220 mg, 62%. (Found: C, 53.1; H, 5.0; N, 8.75. Calc. for $C_{21}H_{23}MoN_3O_4 0.1C_6H_6$ requires C, 53.4; H, 4.9; N, 8.6%). m/z (FAB, for ^{98}Mo): 479 (M$^+$), 451 (M - CO), 423 (M - 2CO), and 365 (M - 2 - 4C0). ^{13}C−{$_1$H}NMR (62.9 MHz. $CDCl_3$) δC: 15.3 (1C, s, methyl carbon from fench residue), 18.1 (1C, s, methyl carbon from fench residue), 18.9 (1C, s, methyl carbon from fench residue), 23.8 (1C, s, methyl carbon from fench residue), 26.7 (1C, s, methyl carbon from fench residue), 45.8

(1C, s, acetyl carbon), 124.0 (1C, s, pyridyl carbon with H), 124.6 (1C, s, pyridyl carbon with H), 137.1 (1C, s, pyridyl carbon with H), 153.0 (1C, s, pyridyl carbon with H), 222.5 (1C, s, $\mathrm{Mo\underline{C}O}$), 223.9 (1C, s, $\mathrm{Mo\underline{C}O}$), 224.6 (1C, s, $\mathrm{Mo\underline{C}O}$) and 233.5 (1C, s, $\mathrm{Mo\underline{C}O}$).

The following two compounds were prepared in a similar to the method to prepared (5).

$[\mathrm{Cr(fench{=}NN{=}CMe)C_5H_5N}]$ (6)

The azine chromium(0) complex (6) was prepared in 66% yield by addition of $[\mathrm{Cr(C0)_4(nbd)}]$ to (4). (Found: C, 58.61; H, 6.65; N, 8.75. Calc. for $C_{21}H_{23}CrN_3O_4$ requires C, 58.2; H, 5.35; N, 9.7%). m/z (FAB, for ^{52}Cr): 433 (M^+), 377 (M - 2CO), 349 (M - 3CO), and 321 (M - 4C0).

$[\mathrm{W(fench{=}NN{=}CMe)C_5H_5N}]$ (7)

The azine chromium(0) complex (6) was prepared in 55% yield by addition of $[\mathrm{W(C0)_4(nbd)}]$ to (4). (Found: C, 44.4; H, 4.4; N, 7.2. Calc. for $C_{21}H_{23}N_3O_4W$ requires C, 44.6; H, 4.1; N, 7.4%). m/z (FAB, for ^{184}W): 565 (M^+), 537 (M - CO), 507 (M - 2 - 2CO), 481 (M - 3C0) and 453 (M - 4C0).

$[\mathrm{PdCl_2(Fench{=}NN{=}CMe)C_5H_5N}]$ (8)

A solution containing (4), (392 mg, 0.14 mmol) and $[\mathrm{PdCl_2(NCPh)_2}]$ (557 mg, 0.14 mmol) in dichloromethane (5 cm^3) was put aside for 24 h. The solvent was then removed and methanol added to the residue to give (8) as an orange solid. Yield 456 mg, 70%. (Found: C, 44.6; H, 4.95; N, 8.9. Calc. for $C_{17}H_{23}Cl_2N_3Pd.0.3CH_2Cl_2$ requires C, 44.0; H, 5.1; N, 8.9%). m/z (FAB, for ^{106}Pd and ^{35}Cl): 411 (M + 1 - Cl) and 373 (M - 2 - 2Cl).

$[\mathrm{PdBr_2(fench{=}NN{=}CMe_2C_5H_5N}\ ]$ (9)

A solution containing (8) (250 mg, 0.06 mmol) and LiBr (1.41 g, 0.013 mol) in acetone (20 cm3) and was put aside for 15 h. The solvent was then removed and methanol added to the residue to give (9) as a yellow solid. Yield 148 mg, 50%. (Found: C, 38.05; H, 4.1; Br, 30.1; N, 7.5. Calc. for $C_{17}H_{23}Br_2N_3Pd$ requires C, 38.1; H, 4.3; Br, 29.8; N, 7.8%). m/z (FAB, for ^{106}Pd and ^{35}Cl): 535 (M + 2), 454 (M-Br).and 374 (M-1-2Br).

$[\mathrm{PdI_2(fench{=}NN{=}CMe)C_5H_5N}]$ (10)

A solution containing (8) (135 mg, 0.3 mmol) and NaI (1.061 g, 709 mmol) in acetone (20 cm^3) and was put aside for 15 h. The solvent was then removed and methanol added to the residue to give (9) as a yellow solid. Yield 151 mg, 79%. (Found: C, 31.7; H, 3.5; N, 6.3. Calc. for $C_{17}H_{23}I_2N_3Pd.0.3CH_2Cl_2$ requires C, 31.7; H, 3.6; N, 6.4%). m/z (FAB, for ^{106}Pd and ^{35}Cl): 629 (M + 2), 502 (M - I) and 374 (M - 1 -2I).

$[(\eta^3\text{-}2\text{-}\mathrm{MeC_3H_4})\mathrm{Pd(fench{=}NN{=}CMe)C_5H_5N]\ PF_6}]$ (11)

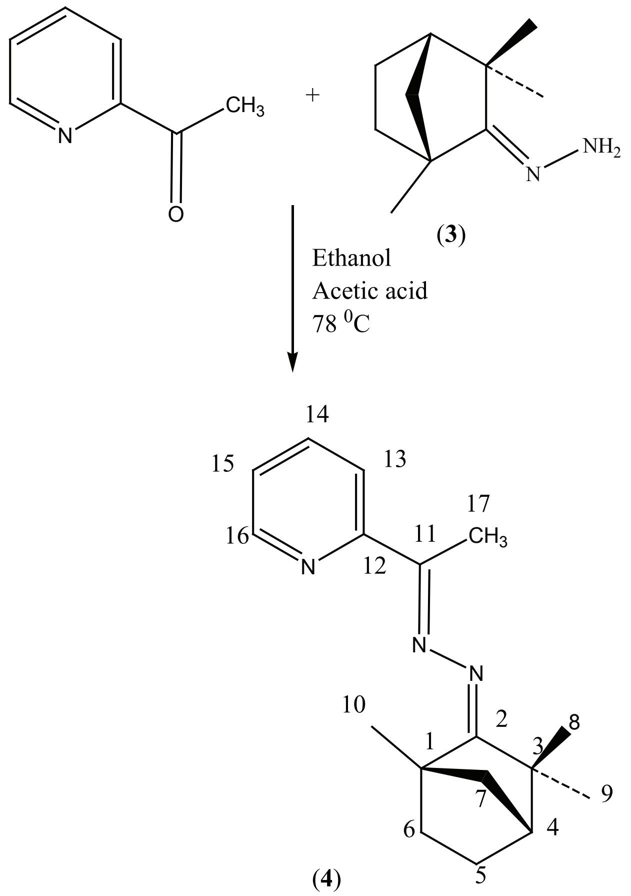
A solution containing (8) (672 mg, 1.36 mmol) and [PdCl$_2$(η^3-2-MeC$_3$H$_4$)$_2$] (111 mg, 0.28 mmol) in dichloromethane (10 cm^3) was put aside for 3 h. The solvent was then evaporated to low volume under reduced pressure and NH$_4$PF$_6$ (665 mg, 16.88 mmol) in methanol was added to the residue to give (11) as pale green microcrystals.Yield 130 mg, 80%. (Found: C, 43.7; H, 5.1; F, 19.7; N, 7.1. Calc. for $C_{21}H_{30}F_6N_3PPd$ requires C, 43.8; H, 5.25; F, 19.8; N, 7.39%). m/z (FAB, for ^{106}Pd and ^{35}Cl): 430 (M – PF$_6$). ^{13}C−{^{1}H}NMR (62.9 MHz. CDCl$_3$) δC: 14.8 (1C, s, methyl carbon from fench residue), 17.1 (1C, s, methyl carbon from fench residue), 26.7 (1C, s, methyl carbon from fench residue), 48.6 (1C, s, $\underline{\text{Me}}$C3H4), 52.34 (1C, s, acetyl carbon), 61.9 (2C, br, $\underline{C}$=C=$\underline{C}$), 125.5 (1C, s, pyridyl carbon with H), 125.6 (1C, s, pyridyl carbon with H), 141.2 (1C, s, pyridyl carbon with H) and 147.9 (1C, s, pyridyl carbon with H).

Result and Discussion

The diimine (4) was prepared by heating 2-diacetylpyridine with fenchone hydrazone (3) in boiling ethanol in the presence of acetic acid as the catalyst for 5 h [Scheme 1 which also shows the numbering for (4)]. The product was isolated as white solid in 85% yield. The diimine ligand (4) has been fully characterized by (i) elemental analysis (C, H, N); (ii) the infrared spectrum, which showed a band at 1642 cm^{-1} due to ν(C=N) (Table 1); (iii) mass spectrometry, which showed a parent molecular ion at m/z = 269 and (iv) the ^{1}H NMR spectrum (Table 2).

The NMR assignments for the protons and carbons for the diimine (4) were made after comparison with the literature values (Kolehmainen *et. al.*, 1990 and Shaw *et. al.*, 1995). In the ^{1}H NMR spectrum of (4) the resonances of the three methyl protons from the fenchone residue were singlets at 1.17, 1.19 and 1.34 ppm (Table 2). The resonance of the $C\underline{H}_3$C=N protons was a singlet at 2.34 ppm.

The resonances of the pyridyl protons gave a broad doublet at 8.62 ppm (H^{16}), a doublet of triplets at 8.15 ppm (H^{13}), a doublet of triplets at 7.75 ppm (H^{14}) and a multiplet at 7.32 ppm (H^{15}). The ^{13}C-{^{1}H} NMR spectrum of (4) was also recorded and the resonances assigned with the aid of an Attached Ptoton Test (APT), and DEPT-135 experiments. The resonances for the three methyl carbons from the fenchone residue were singlet at 12.8, 17.2 and 22.2 ppm. The $\underline{C}H_3$C=N carbons resonated at 51.0 ppm and four singlets at 148.4, 135.8, 123.4 and 120.5 ppm were assigned to pyridyl carbons containing hydrogen.



Scheme 1 Synthesis of 2-diacetylpyridine-(1*R*)-(-)-fenchone azine (4)

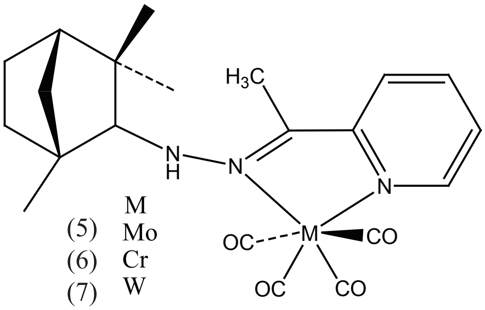
The diimine (4) been investigated as a ligand for group 6 metal carbonyls. Treatment of $[Mo(CO)_4(nbd)]$ with (4) in benzene at 80°C gave the molybdenum(0) complex (5) which was isolated as an intense red-brown solid. The intense-brown coloration suggest that the N=CH_CH=N group is coordinated to the metal, forming a five-membered ring (Van Koten & Vrieze, 1982; Zassinovich, *et. al*., 1992 and Shaw *et. al*., 1994). The infrared absorption bands at 2010, 1920 and 1854 cm^{-1} were in the expected region for a tetracarbonyl complex and the formulation was further supported by mass spectrum which showed four sequential losses of carbonyl ligands with peaks at 479 (M^+), 451(M - CO), 423 (M - 2CO) and 365 (M - 2 - 4CO) (11).

The 1H and $^{13}C\text{-}\{^1H\}$ NMR spectra of (5) showed the presence of two related species, in the approximate ratio of major:minor of 7:1. Only the chemical shifts of the predominat species that is the one present with relative intensity 7 are given in Table 2. Some of the chemical shifts for the minor specie are given in Table 3. We consider that the two species are rotamers.

In the ^{1}H NMR spectrum of (5) the resonances of the three fenchone methyl protons were singlets at 1.16, 1.29 and 1.34 ppm and a singlet at 2.32 ppm was assigned to the resonance for the $C\underline{H}_3C=N$ protons (Table 2). Three resonances which occurred (i) at

9.05(d) ppm, (ii) in the region 7.2-7.98 (m) ppm and (iii) 7.31-7.65 ppm were assigned to the pyridyl protons.

The ^{13}C-{^1H} NMR spectrum of (5) the resonances of the $\underline{C}\equiv O$ carbons were singlets at 224.6, 223.5 and 222.5 ppm and supported the formulation of (5) as a tertracarbonyl complex. The resonances for fenchone methyl and $\underline{C}H_3C=N$ carbons were singlets at 18.8, 23.8, 26.7 and 45.8 ppm respectively. The resonances for the pyridyl carbons were singlets at 123.0, 124.6, 137.1 and 153.0 ppm.



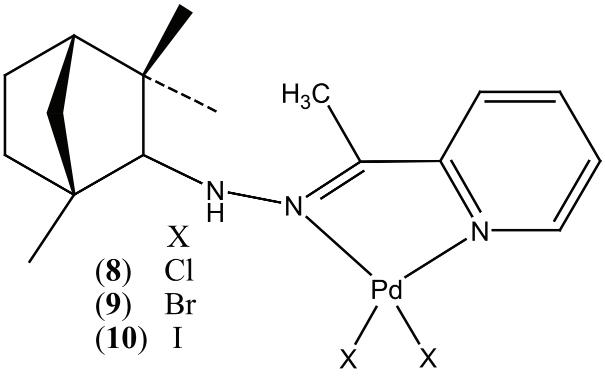
The analogous tetracarbonylchromium(0) complex (6) and tetracarbonyltungsten(0) complex (7) were prepared similarly by treatment [Cr(CO)$_4$(nbd)] or [W(CO)$_4$(nbd)] with (4). The ^{1}H NMR spectrum of (6) showed the presence of three related species, in the approximate ratio of major : minor of 8 : 3 : 1 and for (7) two species were observed in the ratio of 8:1. We again consider that these species are rotamers. The ^{1}H, mass spectral and infrared data of (6) and (7) were analogous to tetracarbonylmolybdenum(0) complex (5), thus we envisage them to have the same five-membered chelate ring.

We also studied the coordination behaviour of ligand (4) with palladium.The dichloropalladium(II) complex (8) was obtained as a yellow solid when we treated (4) with [PdCl$_2$(NCPh)$_2$] in dichloromethane. The infrared spectrum of (8) showed bands at 275 and 345 cm^{-1} due to ν(Pd-Cl) (Table 1.0). In the mass spectrum we could see the loss of two chloride atoms that is peaks at 411 (M - Cl), and 377 (M + 1 - Cl). Electrical conductivity measurements of (8) at 20°C in acetone solution showed it to be a non-electrolyte (molar conductivity, Λ_m = 1.4 ohm^{-1} mol^{-1} cm^2) (Geary,1971).

In the NMR spectrum of (8) we could see three species present in the approximate ratio of 1:1:2. The chemical shifts of the predominant species, that is one present with relative intensity 2, are give in Table 2.

In the ^{1}H NMR spectrum of (8) the resonances of the three fenchone methyl protons were singlets at 1.22, 1.32 and 1.39 ppm (Table 2). The resonance $C\underline{H}_3C=N$ protons was a singlet at 2.44 ppm. The resonances for the pyridyl protons were multiplets at 7.55, 7.85, 8.25 and 9.12 ppm. In the ^{13}C-{^1H} NMR spectrum of (9) the resonances for $\underline{C}$H3C=N was singlets at 46.0 ppm. The resonances for the pyridyl carbons were singlets at 125.7, 127.0.141.0 and 150.6 ppm. We could not assign resonances for methyl carbons from fenchone residue since the signals from the various rotamers were very close to each other.

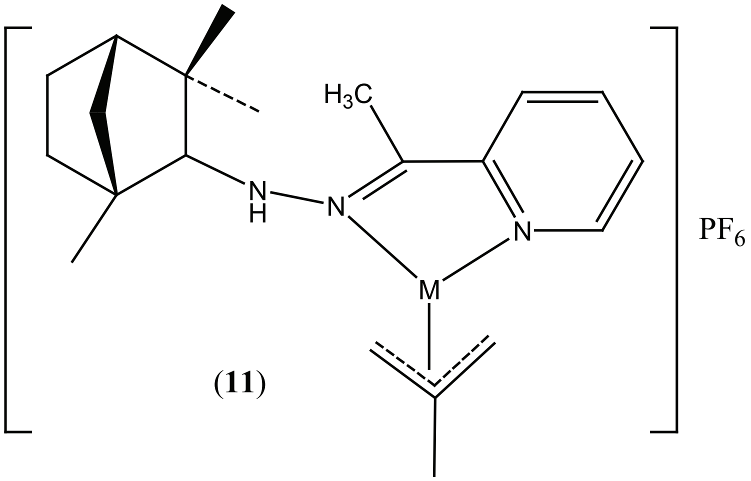
The corresponding bromo-(9) and chloro-(10) complexes were prepared from chloro-complex (8) by metathesis. Treatment of an acetone solution of (8) with lithium bromide or sodium iodide gave the corresponding bromopalladium (9) or iodopalladium complex (10), respectively.



X
(8) Cl
(9) Br
(10) I

Treatment of (4) with $[\{(\eta^3\text{-}2\text{-MeC}_3\text{H}_4)\text{PdCl}_2\}_2]$ in dichloromethane gave the chloride salt which was converted to the corresponding PF$_6$ salt (11). In the mass spectrum we could see peaks for the molecular ion m/z = 430 which corresponded to the loss of the chloride atom {430 (M - Cl)}. Electrical conductivity measurements of (11) at 20 ^{0}C in acetone solution showed it to be 1:1 electrolyte (molar conductivity, Λ_m = 101 ohm^{-1} mol^{-1} cm^2) (Geary,1971).

In the ^{1}H NMR spectrum of (11) the resonances of the allyl protons were broad due to the fluxional process even at -50^{o}C. The H$_{anti}$ and H$_{syn}$ protons of the allyl resonated as broad peaks at 2.95, 3.32, 3.38 and 413 ppm. The resonances C$\underline{H}_3$C=N and methyl protons from the allyl residue were singlets at 2.36 and 2.18 ppm, respectively. The resonances for the methyl protons from the fenchone residue were singlets at 1.25, 1.30, and 1.41 ppm. The pyridyl protons resonated as multiplets at 7.72, 7.97, 8.15 and 8.85 ppm.



(11)

Table 1 Infrared data

	IR bands (cm^{-1})		
Compound	v(C=N)^a	v(M−C1)^b	c(C≡O)^c
(4)	1642(m)	-	
(5)	1655(m)	-	2010, 1912(s),1854(s)
(6)	1655(m)	-	2008(s), 1910(s), 1849(s)
(7)	1654(m)	-	2004(s), 1930(s), 1850(s)
(8)	1645(m)	275(m), 245(m)	-
(9)	1640(m)	-	-
(10)	1628(m)	-	-
(11)	1645(m)	-	-

In the ^{13}C-{^1H} spectrum of (11) the resonances for the three methyl carbons from the fenchone residue were singlet at 14.8, 17.1 and 26.7 ppm. The $C\underline{H}_3C=N$ carbons and methyl carbons from the allyl residue resonated as singlets at 52.3 and 48.6 ppm, respectively. Resonances for the carbons of H_{anti} and H_{syn} gave a broad peak centred at 61.9 ppm.

Table 2 Proton NMR data

	δ(acetyl)	δ(pyridyl)	δ(fenchone methyl	other
(4)	2.34(3H, s)	7.32(m)	1.17(3H,s)	-
	-	7.75(m)	1.19(3H,s)	-
	-	8.15(m)	1.34(3H,s)	-
	-	8.62(d)	-	-
(5)	2.34(3H,s)	7.31(m)	1.16(3H,s)	-
	-	7.72-7.98(2H,m)	1.29(3H,s)	-
	-	9.05(d)	1.34(3H,s)	-
(6)	2.27(3H,s)	7.60(d)	1.14(3H,s)	-
	-	8.12(m)	1.29(3H.s)	-
	-	8.62(dd)	1.38(3H,s)	-
	-	9.20(bd)	-	-
(7)	2.34(3H.s)	7.35(m)	1.14(3H,s)	-
	-	7.66-7.98(2H,m)	1.30(3H,s)	-
	-	9.23(d)	1.36(3H,s)	-
(8)	2.44(3H,s)	7.55(m)	1.48 - 0.98	-
	-	7.85(m)	-	-
	-	8.25(m)	-	-
	-	9.12(m)	-	-
(9)	2.37(3H,s)	7.52(m)	1.57-0.93	-
	-	7.85(m)	-	-
	-	8.15(m)	-	-
	-	9.46(m)	-	-
(10)	2.37(3H,s)	7.55(m)	1.60-0.90	-
(11)	-	7.75(m)	-	-
	-	8.15(m)	-	-
	-	9.85(m)	-	-

Table 2 (cont.)

	δ(acetyl)	δ(pyridyl)	δ(fenchone methyl	other
(11)	7.72(m)	1.41(3H,s)	1.41(s)	2.98(1H, b, H_{anti})
-	7.97(m)	1.32(3H,s)	1.32(s)	3.32(1H, b, H_{anti})
-	8.15(m)	1.25(3H,s)	1.25(s)	3.38(1H, b, H_{syn})
-	8.8(m)	-	-	4.13(1H, b, H_{syn})

[a] Proton NMR recorded at 400 MHz, chemical shift δ relative to SiMe4, solvent CDCl3 unless stated; s=singlet, d=doublet, m=multiplet, t=triplet

Table 3 Some of the 1H NMR data for the rotamer minor products data

	δ(acetyl)	δ(pyridyl)	δ(fenchone methyl	other
(5)	2.24(3H,s)	7.31(m)	1.02(3H,s)	-
	-	7.72-7.98(2H,m)	1.16(3H,s)	-
	-	9.05(d)	1.29(3H,s)	-
(6a)	2,32(2H,s)	7.60(m)	1.17(3H,s)	-
	-	8.12(bd)	1.29(3H,s)	-
	-	8.62(bd)	1.33(3H,s)	-
		9.2(bd)		
(6b)	2.24(3H,s)	7.60(d)	1.10(3H,s)	-
	-	8.12(m)	1.29(3H,s)	-
	-	8.62(dd)	1.25(3H,s)	-
	-	9.20(dd)	-	-
	2.29(3H,s)	7.35(m)	1.04(3H,s)	-
	-	7.66-7.98(2H,m)	1.25(3H,s)	-
	-	9.23(d)	1.22(3h,s)	-

[a] Proton NMR recorded at 400 MHz, chemical shift δ relative to SiMe4, solvent CDCl3 unless stated; s=singlet, d=doublet, m=multiplet, t=triplet

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