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Synthesis and reactivity of new methylallylpalladium(II) complexes with bidentate 2-(methylthio-*N*-benzylidene)anilines

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Abstract

This work describes the synthesis, characterisation and reactivity of new methylallyl Pd(II) complexes that contain bidentate 2-(methylthio-*N*-benzylidene)anilines as ligands. The reaction of the binuclear complex $[(\eta^3\text{-Me-allyl})Pd(\mu\text{-Cl})_2]$ with $AgBF_4$ causes the total abstraction of the chloride bridges, with the subsequent formation of an intermediary fragment of Pd(II). This fragment in turn reacts with neutral bidentate 2-(methylthio-*N*-benzylidene)anilines to give cationic complexes of Pd(II) of general formula $[(\eta^3\text{-Me-allyl})Pd(\eta^2\text{-}S,N\text{-}MeSC_6H_4N{=}CHC_6H_4(X)Y)]BF_4$ [X = H, Y = H (**1**); X = F, Y = H (**2**); X = Me, Y = H (**3**); X = H, Y = Cl (**4**); X = H, Y = Me_2N (**5**); X = H, Y = NO_2 (**6**)]. The new complexes were characterised by means of elemental analysis, IR, NMR [^1H, $^{19}F\{^1H\}$, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, Dept, ^1H–^1H-COSY, HSQC, HMBC] and mass spectroscopies. The reaction of the Pd(II) complexes with nucleophiles such as NaI, $(EtO)_2PS_2K$, KCN, KSCN or NaH lead to the deco-ordination of the bidentate ligands to give dimeric or polymeric complexes of Pd(II). The reactivity pattern observed is discussed by a theoretical analysis based on Fukui functions.

Keywords: Palladium; 2-(Methylthio-*N*-benzylidene)anilines complexes; Schiff base complexes; Methylallylpalladium complexes; NMR spectra

1. Introduction

Transition metal complexes containing heterodifunctional bidentate ligands that present hard and soft donor sites are expected to be efficient in some catalytic transformations [1]. In particular, complexes containing thioether derivatives with N,S-; As,S- or P,S-donor sets as ligands have been extensively studied. Due to the thioether function the ligand is expected to be more labile, permitting the formation of a vacant site at the metal centre [2]. These complexes also show the ability to transfer the alkyl group from the thioether to suitable nucleophiles, and be converted into thiolate complexes [3].

In 1995, Basuli et al. [4] studied the co-ordination properties of Schiff bases derived from substituted benzylideneanilines, of class $[p\text{-}XC_6H_4CH{=}NC_6H_4(2\text{-}SMe)]$ (X = H, Me, OMe, Cl, NO_2). These ligands react with palladium(II) acetate to produce a cyclopalladation reaction. In this sense, Schiff bases are suitable ligands for cyclopalladation or mercuration reactions [5].

In this work, we report the synthesis and characterisation of new mononuclear cationic complexes of palladium(II) of the type $[(\eta^3\text{-Me-allyl})Pd(\eta^2\text{-}S,N\text{-}MeSC_6H_4N{=}CHC_6H_4(X)Y)]BF_4$ where X = H, Y = H (**1**); X = F, Y = H (**2**); X = Me, Y = H (**3**); X = H, Y = Cl (**4**); X = H, Y = Me_2N (**5**) and X = H, Y = NO_2 (**6**)]. The reactivity of the S–C bond of the thioether group of the Schiff base toward nucleophilic attack is discussed. Theoretically, by analysing the corresponding Fukui functions [6–8], the reactivity of the different sites of the molecule with regard to nucleophilic, electrophilic or free radical attack is analyzed. The latter study sheds light on the reactivity behaviour of the palladium(II) cationic complexes reported in the present work.

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2. Experimental

2.1. General

All reactions were carried out under purified nitrogen by using Schlenk-tube techniques. The solvents used in the reactions were of analytical grade and, in some cases of reagent grade, and were dried by a reported procedure [9]. The 2-(methylthio)-*N*-substituted-benzylidene) anilines were synthesised according to standard procedures by condensing equimolar amounts of 2-(methylthio)aniline and the respective substituted benzaldehyde, under continuous stirring for 2 h, in the presence of magnesium sulfate [10]. The compounds [(η^3-Me-allyl)Pd(μ-X)]$_2$ (X = Cl, I) [11,12] and [$(EtO)_2PS_2K$] [13] were prepared following literature methods.

NMR spectra were recorded on Bruker AC-200P and Avance-400 spectrometers. Chemical shifts are reported in ppm relative to Me_4Si (^{1}H) and 85% H_3PO_4 ($^{31}P\{^1H\}$, positive shifts downfield). The IR spectra in the range 4000–250 cm^{-1} were recorded in KBr pellets on a model Vector-22 FT-IR Bruker spectrophotometer. Elemental analyses (C, H, N, S) were made with a Fisons model EA-1108 microanalyser. FAB mass spectral analyses were performed in a VG Autospec spectrometer with 3-nitrobenzylalcohol as a matrix. Conductivity measurements were carried out in solution, using a WTW LF-521 conductimeter with a cell of constant 1.07.

2.2. Synthesis of complexes

2.2.1. *[(η^3-Me-allyl)Pd(η^2-S,N-$MeSC_6H_4N{=}CHC_6H_4$(X)Y)]BF_4 [X = H, Y = H (**1**); X = F, Y = H (**2**); X = Me, Y = H (**3**); X = H, Y = Cl (**4**); X = H, Y = Me_2N (**5**); X = H, Y = NO_2 (**6**)]*

A solution of [(η^3-Me-allyl)Pd(μ-Cl)]$_2$ (0.25 mmol, 100 mg) in THF (20 cm^3) was treated with $AgBF_4$ (0.51 mmol, 100 mg). The mixture was stirred at room temperature for 2 h and the AgCl formed was filtered off through Kieselguhr. To the resulting solution was added a stoichiometric amount of the corresponding bidentate ligand [L_1: 0.50 mmol, $MeSC_6H_4N{=}CHC_6H_5$ (113.5 mg); $MeSC_6H_4N{=}CHC_6H_4F$ (122.5 mg); $MeSC_6H_4N{=}CHC_6H_4Me$ (120.5 mg); $MeSC_6H_4N{=}CHC_6H_4Cl$ (130.8 mg); $MeSC_6H_4N{=}CHC_6H_4NMe_2$ (135 mg); $MeSC_6H_4N{=}CHC_6H_4NO_2$ (136 mg)], and the mixture stirred at room temperature. The solution was concentrated to a small volume and the complexes were precipitated by the addition of Et_2O. The solid product was collected by filtration, washed with cold THF and Et_2O, and dried under vacuum.

1: Yield: 200 mg (83%). Anal. Found: C, 45.7; H, 4.3; S, 6.5; N, 2.5. Calc. for $C_{18}H_{20}BF_4NPdS$: C, 45.5; H, 4.2; S, 6.7; N, 2.9%. Λ_M = 200 Ω^{-1} mol^{-1}cm^2. ^{1}H NMR in CD_3CN: δ 2.07 [s, 3H, C(allyl)–Me], 2.85 [s, 3H, S–Me], 3.07 [s, 2H, H_{anti}], 3.90 [s, 2H, H_{syn}], 7.46 [dt, 1H, H_4, $^3J(H_4–H_5) = {}^3J(H_4–H_3) = 7.45$ Hz, $^4J(H_4–H_6) = 1.3$ Hz], 7.52 [dt, 1H, H_5, $^3J(H_5–H_4) = {}^3J(H_5–H_6) = 7.45$ Hz, $^4J(H_5–H_3) = 1.4$ Hz], 7.60 [pt, 2H, H_9, H_{11}, $^3J(H_9–H_8) \approx {}^3J(H_9–H_{11}) \approx {}^3J(H_{11}–H_{10}) \approx {}^3J(H_{11}–H_{12}) = 7.5$ Hz], 7.74–7.65 [m, 3H, H_{10}, H_6, H_3], 8.06 [d, 2H, H_8, H_{12}, $^3J(H_8–H_{12}) \approx {}^3J(H_{12}–H_{11}) = 7.3$ Hz], 9.09 [s, 1H, $CH_7{=}$N]. FT-IR (KBr, cm^{-1}): ν(CN), 1610 vs, $\nu(BF_4)$, 1057 vs, 521 m. MS (FAB$^+$) *m*/*z* 388 (M^+–BF_4).

2: Yield: 198 mg (79%). Anal. Found: C, 43.9; H, 4.1; S, 6.3; N, 2.6. Calc. for $C_{18}H_{19}BF_5NPdS$: C, 43.8; H, 3.8; S, 6.5; N, 2.8%. Λ_M = 112.8 Ω^{-1} mol^{-1} cm^2. ^{1}H NMR in CD_3CN; δ 2.04 [s, 3H, C(allyl)–Me], 2.83 [s, 3H, S–Me], 3.07 [s, 2H, H_{anti}], 3.96 [s, 2H, H_{syn}], 7.34 [dd, 1H, H_{11}, $^3J(H_{11}–H_{10}) = 9.3$ Hz, $^4J(H_{11}–H_9) = 1.6$ Hz] 7.43 [dd, 1H, H_8, $^3J(H_8–H_9) = 7.4$ Hz, $^4J(H_{11}–H_9) = 1.9$ Hz], 7.50 [m, 2H, H_3, H_4], 7.64 [m, 2H, H_5, H_6], 7.74 [dpt, 1H, H_{10}, $^3J(H_{10}–H_{11}) \approx {}^3J(H_{10}–H_9) \approx 7.4$ Hz, $^4J(H_{10}–H_8) = 1.9$ Hz], 8.21 [dt, 1H, H_9, $^3J(H_9–H_8) \approx {}^3J(H_9H_{10}) = 7.5$ Hz], 9.18 [s, 1H, $CH_7{=}$N].^{19}F NMR in CD_3CN: δ −115.8 [s, F-ring]. FT-IR (KBr, cm^{-1}): ν(CN), 1621 vs, $\nu(BF_4)$, 1060 vs, 521 m. MS (FAB$^+$) *m*/*z* 406 (M^+–BF_4).

3: Yield: 168 mg (65%). Anal. Found: C, 46.4; H, 4.7; S, 6.3; N, 3.1. Calc.for $C_{19}H_{22}$ BF_4NPdS: C, 46.6; H, 4.5; S, 6.5; N, 2.9%. ^{1}H NMR in CD_3CN: δ 2.02 [s, 3H, C(allyl)–Me], 2.57 [s, 3H, C–Me], 2.91 [s, 3H,S–Me], 2.02 [s, 2H, H_{anti}], 3.85 [s, 2H, H_{syn}], 7.41 [d, 1H, H_{11}, $^3J(H_{11}–H_{10}) = 8.2$ Hz], 7.43 [pt, 1H, H_9, $^3J(H_9–H_8) \approx {}^3J(H_9–H_{10}) = 8.1$ Hz], 7.56 [m, 3H, H_4, H_5, H_{10}], 7.75 [dd, 1H H_3, 3J(H_3–H_4) = 7.5 Hz, $^4J(H_3–H_5) = 1.5$ Hz], 7.78 [dd, 1H, H_6, $^3J(H_6–H_5) = 7.5$ Hz, $^4J(H_6–H_4) = 1.3$ Hz], 7.95 [d, 1H, H_8, $^3J(H_8–H_9) = 7.6$ Hz], 9.37 [s, 1H, $CH_7{=}$N]. FT-IR (KBr, cm^{-1}): ν(CN), 1610 vs, $\nu(BF_4)$, 1056 vs, 521 m. MS (FAB$^+$) *m*/*z* 402 (M^+–BF_4).

4: Yield: 168 mg (65%). Anal. Found: C, 41.3; H, 3.6; S, 6.2; N, 2.7. Calc. for $C_{18}H_{19}BClF_4NPdS$: C, 41.1; H, 3.6; S, 6.1; N, 2.6%. ^{1}H NMR in CD_3CN; δ 2.08 [s, 3H, C(allyl)–Me], 2.88 [s, 3H, S–Me], 3.11 [s, 2H, H_{anti}], 3.97 [s, 2H, H_{syn}], 7.49 [dt, 1H, H_4, $^3J(H_4–H_3) \approx {}^3J(H_4–H_5) = 7.5$ Hz; $^4J(H_4–H_6) = 1.3$ Hz], 7.54 [dt, 1H, H_5, $^3J(H_5–H_4) \approx {}^3J(H_5–H_6) = 7.6$ Hz, $^4J(H_5–H_3) = 1.5$ Hz], 7.63 [d, 2H, Hb,Hb′, AA′BB′ system: ^3J(Ha–Hb) = ^3J(Ha′-Hb′) = 8.5 Hz], 7.69 [dd, 1H, H_3, $^3J(H_3–H_4) = 7.6$ Hz, $^4J(H_3–H_5) = 1.5$ Hz], 7.74 [dd, 1H, H_6, $^3J(H_6–H_5) = 7.6$ Hz, $^4J(H_6–H_4) = 1.2$ Hz], 8.07 [d, 2H, Ha, Ha′, AA′BB′ system: $^3J(HaHb) = {}^3J(Ha'–Hb') = 8.5$ Hz], 9.07 [s, 1H, $CH_7{=}$N]. FT-IR (KBr, cm^{-1}): ν(CN), 1612 vs, $\nu(BF_4)$, 1060 vs, 521 m.

5: Yield: 253 mg (96%). Anal. Found: C, 46.2; H, 4.8; S, 6.3; N, 5.4. Calc. for $C_{20}H_{25}BF_4N_2PdS$: C, 46.3; H, 4.9; S, 6.2; N, 5.4%. ^{1}H NMR in CD_3CN: δ 2.21 [s, 3H, C(allyl)–Me], 2.86 [s, 3H, S–Me], 3.13 [s, 6H, NMe_2], 3.18 [s, 2H, H_{anti}], 4.07 [s, 2H, H_{syn}], 6.85 [d, 2H, Hb,Hb′, AA′BB′ system: $^3J(Ha–Hb) = {}^3J(Ha'–Hb') = 9.0$ Hz],

7.40 [dt, 1H, H_4, $^3J(H_4–H_3) \approx {}^3J(H_4–H_5) = 7.7$ Hz; $^4J(H_4–H_6) = 1.1$ Hz], 7.51 [dt, 1H, H_5, $^3J(H_5–H_6) \approx {}^3J(H_5–H_4) = 8.0$ Hz, $^4J(H_5–H_3) = 1.2$ Hz], 7.67 [dd, 1H, H_3, $^3J(H_3–H_4) = 7.7$ Hz, $^4J(H_3–H_5) = 1.2$ Hz], 7.68 [d, 1H, H_6, $^3J(H_6–H_5) = 8.0$ Hz], 8.02 [d, 2H, Ha, Ha′, AA′BB′ system: $^3J(HaHb) = {}^3J(Ha'–Hb') = 9.0$ Hz], 8.83 [s, 1H, CH_7=N]. FT-IR (KBr, cm^{-1}): ν(CN), 1591 vs, $\nu(BF_4)$, 1051 vs, 521 m. MS (FAB^+) *m/z* 431 ($M^+–BF_4$).

6: Yield: 131 mg (65%). Anal. Found: C, 45.3; H, 3.6; S, 5.8; N, 5.1. Calc. for $C_{18}H_{19}BF_4N_2O_2PdS$: C, 41.5; H, 3.7; S, 6.2; N, 5.4%. ^{1}H NMR in CD_3CN: δ 2.08 [s, 3H, C(allyl)–Me], 2.7 [s, 3H, S–Me], 3.10 [s, 2H, H_{anti}], 4.03 [s, 2H, H_{syn}], 7.45 [m, 2H, H_3, H_4], 7.52 [m, 1H, H_6], 7.58 [m, 1H, H_5], 8.22 [d, 2H, Ha, Ha′, AA′BB′ system: $^3J(Ha–Hb) = {}^3J(Ha'–Hb') = 8.8$ Hz], 8.39 [d, 2H, Hb, Hb′, AA′BB′ system: $^3J(Ha–Hb) = {}^3J(Ha'–Hb') = 8.8$ Hz], 8.98 [s, 1H, CH_7=N]. FT-IR (KBr, cm^{-1}): ν(CN), 1616 vs, $\nu(BF_4)$, 1060 vs, 521 m. MS (FAB^+) *m/z* 433 ($M^+–BF_4$).

2.3. Reactivity studies

2.3.1. Reaction of complexes 1–6 with NaI

To a solution of the cationic complexes [(η^3-Me-allyl)Pd(η^2-*S*,*N*-$MeSC_6H_4N$=CHC_6H_4R')]BF_4 [0.50 mmol: R′ = H (**1**; 237.7 mg); F (**2**; 246.7 mg); Me (**3**; 244.8 mg); Cl (**4**; 255 mg); NMe_2 (**5**; 259.2 mg); NO_2 (**6**; 260.2 mg)] in Me_2CO (20 cm^3), a stoichiometric amount of NaI (0.50 mmol, 75 mg) was added, and the mixture stirred at room temperature for 24 h. The solvent was evaporated under reduced pressure and the solid dissolved in the minimum amount of Et_2O. The resulting solution was allowed to stand at −25 °C for 72 h. Two type of crystals were formed (yellow and orange) which were collected by filtration, washed with cold Et_2O, and dried under vacuum. The ^{1}H NMR spectroscopic data of the orange crystals correspond to the free ligand ($MeSC_6H_4N$=CHC_6H_4R') while the yellow crystals correspond to the neutral complex [(η^3-Me-allyl)Pd(μ-I)]$_2$ [^{1}H NMR in $CDCl_3$; δ 1.94 (s, 3H,C(allyl)–Me), 4.13 (s, 2H, H_{sym}), 3.06 (s, 2H, H_{anti}). FAB mass spectrum: {(^{3}-Me-allyl)Pd(μ-I]}$_2^+$, *m/z* 578 (M^+), 451 (M^+–I) [11].

2.3.2. Reaction of complexes 1–6 with [(EtO)$_2$PS$_2$K]

To a solution of complex [(η^3-Me-allyl)Pd(η^2-*S*,*N*-$MeSC_6H_4N$=CHC_6H_4R')] BF_4 [0.50 mmol, R′ = H (**1**; 237.7 mg); F (**2**; 246.7 mg); Me (**3**; 244.8 mg); Cl (**4**; 255 mg); NMe_2 (**5**; 259.2 mg); NO_2 (**6**; 260.2 mg)] in Me_2CO (20 cm^3) was added a stoichiometric amount of [$(EtO)_2PS_2K$] (0.50 mmol, 114 mg). The mixture was stirred at room temperature for 5 h and filtered through Kieselguhr. The solvent was evaporated under reduced pressure to dryness and the residue dissolved in a minimum amount of Et_2O. The resulting solution was allowed to stand at −25 °C for 72 h. The crystals that formed were collected by filtration, washed with cold Et_2O, and dried under vacuum. The NMR data of the crystals correspond to the free ligands. The filtrate was evaporated to dryness to give a brown–orange solid residue, which was characterised as [(η^3-Me-allyl)Pd{η^2-$S_2P(OEt)_2$}] by comparison with an authentic sample.

Preparation of [(η^3-Me-allyl)Pd{η^2-$S_2P(OEt)_2$}]. To a solution of the binuclear complex [(η^3-Me-allyl)PdCl]$_2${ 0.50 mmol, 200 mg} in Me_2CO (30 cm^3), [$(EtO)_2PS_2K$] (1.01 mmol, 228 mg) was added. The mixture was stirred at room temperature for 5 h and the KCl formed filtered off through Kieselguhr. The solution was evaporated to dryness under reduced pressure. The brown orange residue formed was washed with cold Et_2O. This product was dissolved in the minimal amount of $CHCl_3$ and crystallised at room temperature. The product formed was washed with cold Et_2O, and dried under vacuum. Anal. Found: C, 27.3; H, 5.1; S, 1.7. Calc. for $C_8H_{17}O_2PPdS_2$: C, 27.7; H, 4.9; S, 1.9%. ^{1}H NMR in $CDCl_3$: δ 1.36 [t, br, 6H, Me], 1.94 [s, 3H, C(allyl)–Me], 2.76 [s, 2H, H_{anti}], 3.97 [s, 2H, H_{syn}], 4.13 [m, 4H, CH_2–R]. ^{31}P{^{1}H} NMR in $CDCl_3$: δ 103.4 [s, S_2PEt_2].

2.3.3. Reaction of complexes 1–6 with KA (A = CN$^-$, SCN$^-$)

To a solution of the cationic complex [(η^3-Me-allyl)Pd(η^2-*S*,*N*-$MeSC_6H_4N$=CHC_6H_4R')]BF_4 [0.50 mmol: R′ = H (**1**; 237.7 mg); F (**2**; 246.7 mg); Me (**3**; 244.8 mg); Cl (**4**; 255 mg); NMe_2 (**5**; 259.2 mg); NO_2 (**6**; 260.2 mg)] in Me_2CO (20 cm^3), it was added a stoichiometric amount of KA (0.50 mmol, A = CN^-: 33 mg, A = SCN^-: 48.6 mg), and the mixture stirred at room temperature for 5 h. The solution was concentrated under reduced pressure and the white solid formed was eliminated by filtration through Kieselguhr. The resulting solution was allowed to stand at −25 °C. Orange crystals were formed, which were collected by filtration, washed with cold Et_2O, and dried under vacuum. The ^{1}H NMR spectroscopic data of the orange crystals correspond to the free ligand ($MeSC_6H_4N$= CHC_6H_4R'). The insoluble white solid was analysed by IR spectroscopy; it corresponds to a polymer of general formula [(η^3-Me-allyl)Pd(η^1-A)$_x$]$_n$ (ν(CN) = 2116 and ν(SCN) = 2141 cm^{-1}).

2.3.4. Reaction of complexes 1–6 with NaH

To a solution of complex [(η^3-Me-allyl)Pd(η^2-*S*,*N*-$MeSC_6H_4N$=CHC_6H_4R')] BF_4 [0.50 mmol: R′ = H (**1**; 237.7 mg); F (**2**; 246.7 mg); Me (**3**; 244.8 mg); Cl (**4**; 255.0 mg); NMe_2 (**5**; 259.2 mg); NO_2 (**6**; 260.2 mg)] in MeCN (30 cm^3), a stoichiometric amount of NaH (0.50 mmol, 12.0 mg) was added under inert atmosphere and in an ice bath. The mixture was stirred at room temperature for 15 min. The dark solution was concentrated

under reduced pressure and the black solid formed removed by filtration through Kieselguhr. The resulting solution was evaporated to dryness and a red solid residue was formed. The ^{1}H NMR spectroscopic data showed that the residue corresponds to a mixture of products: methyl-allylchloride, free ligand, benzaldehyde and 2-(methylthio)aniline. The insoluble black solid corresponds to metallic palladium.

2.4. Theoretical and computational details

All calculations were performed with the Gaussian 98 package [14]. density functional theory (DFT) was employed with the three-parameter hybrid exchange functional of Becke [15] and the Lee et al. [16] correlation functional (B3LYP). Relativistic effective core potentials (ECPs) for palladium were employed in all B3LYP calculations. The basis set was the standard LANL2DZ included in Gaussian. The geometries were obtained by full geometry optimisation at the B3LYP level. Graphical pictures were obtained with the MOLEKEL program [17].

In the frame of Frontier molecular orbital theory [8c], an electrophilic attack can be explained by the sharing of electrons from the HOMO with the electrophile, while a nucleophilic attack can be seen as the accepting of the nucleophile electrons by the LUMO. Most of the frontier-electron theory of chemical reactivity can be rationalized from DFT. Parr and Yang derived an expression that quantifies the previously described concepts (for a detailed theoretical discussion see [8a–8d] and references therein), by means of the Fukui function, that is defined as follows [8b,8d]:

$$f(r) = \left(\frac{\partial \mu}{\partial v}\right)_N \quad \text{or} \quad f(r) = \left(\frac{\partial \rho}{\partial N}\right)_v. \tag{1}$$

With ρ the electronic density, μ the chemical potential, v the external potential and N is the number of electrons of the system.

Using the finite-difference approximation for the Fukui function, it is possible to rewrite $f(r)$ as a function of measurable quantities, and separate it in three parts: $f(r)^-$. Fukui function for the most probable electrophilic attack sites, $f(r)^+$, Fukui function for the most probably nucleophilic attack sites and $f(r)^\circ$, Fukui function for probable radical attack sites. The expressions that define these indexes are the following:

$$f(r)^- = [\rho(r)_N - \rho(r)_{N-1}] \approx \rho(r)_{\mathrm{HOMO}}. \tag{2}$$

$$f(r)^+ = [\rho(r)_{N+1} - \rho(r)_N] \approx \rho(r)_{\mathrm{LUMO}}. \tag{3}$$

$$f(r)^0 = \frac{f(r)^+ + f(r)^-}{2} = \frac{\rho_{N+1} - \rho_{N-1}}{2} \approx \frac{\rho_{\mathrm{HOMO}} + \rho_{\mathrm{LUMO}}}{2}. \tag{4}$$

3. Results and discussion

The 2-(methylthio)-*N*-substituted-benzylidene)anilines ligands were synthesised according to a general procedure. Typically, a condensation of equimolar amounts of 2-(methylthio)aniline and the respective substituted benzaldehyde was performed under continuous stirring, in the presence of magnesium sulphate. The overall reaction for all the ligands is represented in Scheme 1.

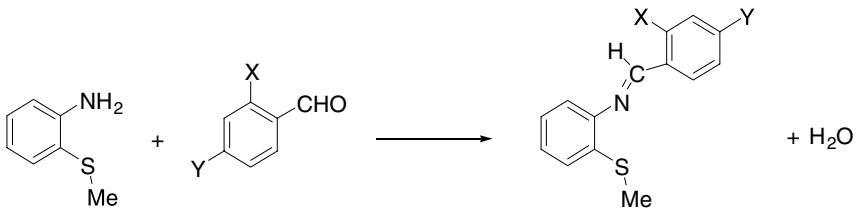
The ligands were characterised by IR and NMR spectroscopies. The infrared spectra show an intense band in the 1600–1680 cm^{-1} range corresponding to the νC=N stretching vibrations. The ^{1}H NMR spectra show a signal at low field (δ 8.28–8.77 ppm) attributed to the iminic proton. A singlet signal is also observed in the δ 2.44–2.48 ppm range, assigned to protons of the methylthioether group [18], together with the characteristic signals of the substituents of the benzylidene group. In the ^{19}F NMR spectrum, the fluorinated derivative shows one singlet signal at −47.7 ppm assigned to the fluorine atom. The ^{13}C NMR spectra of the ligands exhibit the singlet signal corresponding to the carbon of the SMe group in the δ 14.3–14.9 ppm range and a singlet signal of the iminic carbon at δ 156.8–160.4 ppm [18].

The binuclear complex [(η^3-Me-allyl)Pd(μ-Cl)]$_2$ reacted in tetrahydrofuran with silver tetrafluoroborate in a 1:2 molar ratio, forming the probably solvated intermediate species [(η^3-Me-allyl)Pd(THF)$_x$]$^+$. This which reacted further with the different bidentate Schiff bases to give the corresponding palladium(II) cationic complexes [(η^3-Me-allyl)Pd(η^2-*S*,*N*-MeSC$_6$H$_4$N=CHC$_6$H$_4$(X)Y)] BF_4 where X = H, Y = H (**1**); X = F, Y = H (**2**); X = Me, Y = H (**3**); X = H, Y = Cl (**4**); X = H, Y = Me$_2$N (**5**) and X = H, Y = NO$_2$ (**6**)]. This is illustrated in Scheme 2.

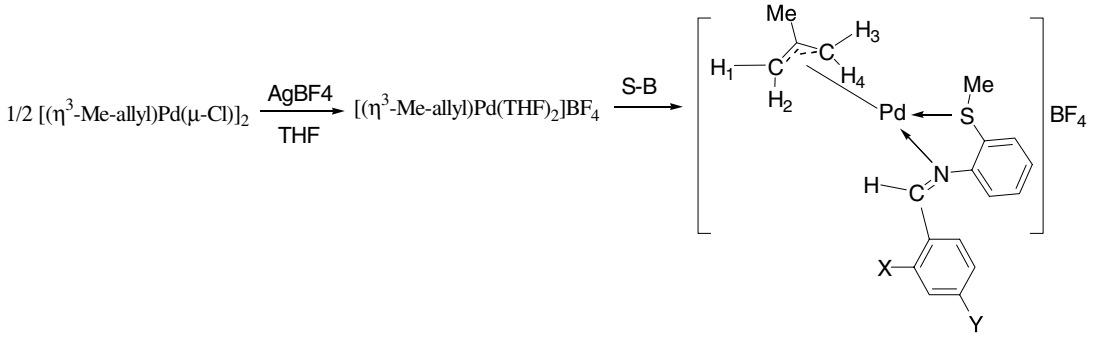
Complexes **1**–**6** were isolated as stable orange solids and characterised by elemental analyses, conductivity measurements, IR, NMR and mass spectroscopies. Complexes behave as 1:1 electrolytes in acetonitrile, with conductivity values in the 113–200 Ω^{-1} cm^2 mol^{-1} range. Their FT-IR spectra in KBr pellets show the presence of the uncoordinated anion, $\nu(BF_4)$ ca. 1060 and 521 cm^{-1}, together with the absorption band corresponding to the C=N group at the 1610–1621 cm^{-1} range.

Selected ^{1}H NMR data of complexes **1**–**6** are summarised in Table 1. The spectra show three singlet resonances at the ranges δ 2.00–2.21, 3.06–3.18 and 3.85–4.14 ppm, attributed to the methyl group, and the methylenic protons H_{anti} and H_{syn} of the co-ordinated methylallyl ligand, respectively [19].

Variable-temperature experiments (295–353 K) show that at high temperature (353 K) occurs a slight broadening of the resonance assigned to the methylene protons of the methylallyl group, probably due to a



Scheme 1. X = H; Y = H, Cl, NMe_2. NO_2, Y = H; X = F, Me.



Scheme 2. X = H; Y = H (**1**); X = F, Y = H (**2**); X = Me, Y = H (**3**); X = H, Y = Cl (**4**), X = H, Y = Me_2N (**5**); X = H, Y = NO_2 (**6**).

Table 1
^{1}H NMR data in CD_3CN for complexes **1**–**6**

Assignment	(**1**)	(**2**)	(**3**)[a]	(**4**)	(**5**)[b]	(**6**)
Me-allyl(H_1)	2.06	2.04	2.00	2.08	2.21	2.08
Hanti	3.06	3.07	3.02	3.11	3.18	3.10
Hsyn	3.89	3.96	3.85	3.97	4.07	4.03
S–Me(H_2)	2.80	2.80	2.90	2.88	2.90	2.70
–N=C–H_7	9.10	9.20	9.4	9.07	8.80	9.00

[a] *ortho*-Me(H_{12}): δ 2.57 ppm.
[b] *p*-NMe_2(H_8): δ 3.13 ppm.

rapid π–σ interconversion of the ligand. This behaviour has been observed for analogous compounds [19d].

Moreover, the complexes show two singlet signal at the ranges δ 2.7–2.9 and 8.8–9.4 ppm, assigned to the methyl protons of the thioether group and an iminic proton, respectively.

The ^{1}H and ^{13}C chemical shifts were assigned with the aid of ^{1}H–^{1}H COSY, DEPT, ^{1}H–^{13}C COSY, HSQC and HMBC experiments. The ^{13}C NMR data and the ^1J(C–H) coupling values are listed in Tables 2 and 3, respectively. The protons and carbon numbering scheme are indicated in Fig. 1.

The ^{13}C assignments were achieved by ^{1}H–^{13}C COSY spectra using HMBC conditions for short or longer range (one-, two- or three-bond correlation). As an example, the ^{1}H–^{13}C HMBC spectrum for complex **5** is shown in Fig. 2. The low field signal correlation clearly shows the assignation of the iminic carbon (C_{12}) at δ 168.4 ppm with the corresponding coupling with the iminic proton [$^1J(C_{12}–H_7) = 164$ Hz]. A strong interaction between C_{14}, $C_{14'}$, C_{13} and C_{11} carbons with the iminic proton H_7 at two or three bonds was observed. Moreover, the spectrum shows a strong correlation between C_{14}, $C_{14'}$, C_{15}, $C_{15'}$ carbons with the H_a, $H_{a'}$ and H_b,$H_{b'}$ protons, with constants coupling values of $^1J(C_{14}–H_a) = {}^1J(C_{14'}–H_{a'}) = 157$ Hz and $^1J(C_{15}–H_b) = {}^1J(C_{15'}–H_{b'}) = 160.7$ Hz, respectively. Fig. 2 shows the assignment of carbons C_4, C_5, C_{17}, C_1 and C_3 at high field with their respective ^1J(C–H) coupling constants (Table 3).

Both figures show the C–H interactions at two- and three-bonds (Table 2). For all complexes these interactions generally show ^3J(C–H) coupling constants values higher than ^2J(C–H). A similar behaviour was observed in trimethylplatinum (IV) complexes [20].

In general, the ^{19}F NMR spectrum of the cationic complexes, show a signal appearing at −150 ppm corresponding to the tetrafluoroborate anion (BF_4^-). Complex (2) shows an additional signal at −115 ppm, assigned to the fluorine atom of the substituted Schiff base.

Finally, the mass spectra of the complexes (FAB^+ mode) show peaks at $m/z = 388$ (**1**), 406(**2**), 402(**3**), 431(**5**) and 433(**6**) (highest relative abundance values of

Table 2
^{13}C NMR data in CD_3CN for complexes **1–6**

Assignment	(**1**)	(**2**)	(**3**)[g]	(**4**)	(**5**)[h]	(**6**)
C1,C3(allyl)	66.4	64.5	65.4	66.0	65.7	65.2
C2(allyl)	132.4	134.9	135.6	135.8	135.4	136.0
C4(*Me*-allyl)	22.9	21.7	22.4	22.4	22.4	22.3
C5(S–Me)	23.6	21.1	23.8	23.1	23.5	19.5
C6	132.1	131.3	130.3	131.4	130.8	132.8
C7	130.5	130.4	130.8	130.7	128.5	129.4
C8	131.2	132.6	132.9	130.5	130.2	128.4
C9	131.0	129.2	139.2	130.1	130.5	128.7
C10	120.7	119.2	120.5	120.2	119.8	119.2
C11	152.1	150.2	151.3	151.2	152.6	149.8
C12(–N=C–)	170.3	161.5	170.2	168.4	168.4	163.6
C13	136.7	123.7(d)[a]	136.2	134.6	121.3	141.9
C14, 14′	130.5	124.6(d)[b]	131.9	131.6	133.0	130.4
C15, 15′	129.9	129.1(d)[c]	126.7	129.5	111.7	124.3
C16	134.2	134.8(d)[d]	144.5	139.2	154.4	150.4
C17	–	115.9(d)[e]	128.8	–	–	–
C18	–	161.8(d)[f]	131.1	–	–	–

[a] $^2J_{CF} = 10.9$ Hz.
[b] $^3J_{CF} = 3.5$ Hz.
[c] $^4J_{CF} = 32.5$ Hz.
[d] $^3J_{CF} = 8.9$ Hz.
[e] $^2J_{CF} = 20.6$ Hz.
[f] $^1J_{CF} = 253.5$ Hz.
[g] 18.9 ppm *ortho*-Me.
[h] 39.8 ppm *p*-NMe_2.

Table 3
Coupling constants ($^1J_{CH}$ in Hz) for complexes **1–6** determined from 2D-NMR (HMBC) spectra

Assignment	(**1**)	(**2**)[a]	(**3**)[b]	(**4**)	(**5**)	(**6**)
^1J(C_1-Hanti)[c]	155	158	158	161	158	159
^1J(C_1-Hsyn)[d]	162	154	161	164	162	162
^1J(C_4–H_1)	129	133	131	130	130	127
^1J(C_5–H_2)	136	146	142	142	139	140
^1J(C_7–H_3)	174	174	172	[e]	175	164
^1J(C_8–H_4)	164	163	165	165	164	162
^1J(C_9–H_5)	144	167	146	161	147	160
^1J(C_{10}–H_6)	161	152	169	158	164	156
^1J(C_{12}–H_7)	169	172	171	168	164	168
^1J{C_{14}–H_8(Ha,a′)}	158	163	163	161[f]	157[f]	162[f]
^1J({C_{15}–H_9(Hb,b′)}	154	159	166	164[g]	161[g]	168[g]

[a] $^1J(C_{16}–H_{10}) = 164$ Hz; $^1J(C_{17}–H_{11}) = 165$ Hz.
[b] $^1J(C_{16}–H_{10}) = 111$ Hz; $^1J(C_{17}–H_{11}) = 163$ Hz.
[c] $^1J(C_1\text{-Hanti}) = {}^1J(C_3\text{-Hanti})$.
[d] $^1J(C_1\text{-Hsyn}) = {}^1J(C_3\text{-Hsyn})$.
[e] Not resolved.
[f] $^1J(C_{14}–H_a) = {}^1J(C_{14'}–H_{a'})$.
[g] $^1J(C_{15}–H_b) = {}^1J(C_{15'}–H_{b'})$.

90–100%), with an isotopic distribution that matched that calculated for a m/e relationship corresponding to $[M^+–BF_4]$.

3.1. Reactivity of complexes *1–6* with nucleophiles

As mentioned in the introduction, transition metal complexes that contain ligands with a thioether group show the ability to transfer the methyl group from the thioether to suitable nucleophiles [3,21]. These properties were analysed for complexes **1–6**, in order to compare their behaviour with previously studied compounds. These were treated with different nucleophiles such as NaI, $(EtO)_2PS_2K$, KCN, KSCN and NaH. The products obtained by these reactions are collected in Scheme 3.

Thus, the reaction with NaI in acetonitrile gives the corresponding free ligand and the binuclear complex

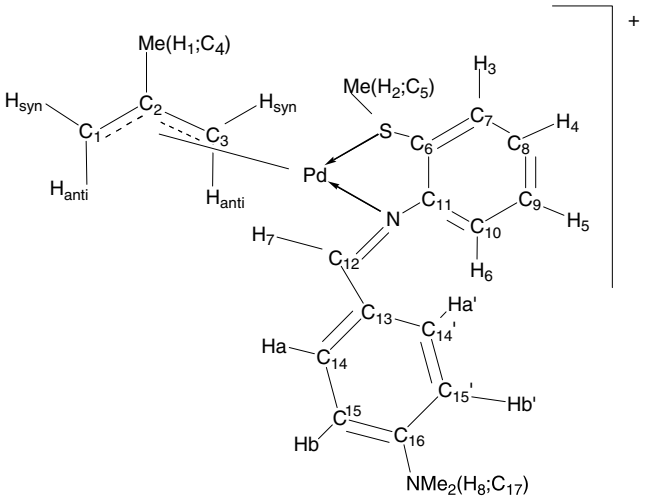


Fig. 1. Proton and carbon atoms numbering for complex **5**.

$[(\eta^3\text{-Me-allyl})Pd(\mu\text{-I})]_2$. These compounds were characterised by NMR and mass spectroscopy. On the other hand, the reactions of the complexes with $(EtO)_2PS_2K$ in acetone afford a brown–orange solid which was characterised as the neutral complex $[(\eta^3\text{-Me-allyl})Pd\{\eta^2\text{-}S_2P(OEt)_2]$, demonstrating the displacement of the N,S-donor ligand. The neutral complex was characterised by comparison with a sample prepared by the reaction of the complex $[(\eta^3\text{-Me-allyl})Pd(\mu\text{-I})]_2$ with $[(EtO)_2PS_2K]$ in acetone. The brown–orange crystals obtained exhibit the expected signals in the ^1H NMR spectrum in the required proportions of the proposed formula. The $^{31}P\{^1H\}$ NMR spectrum shows a signal at δ 103.4 ppm corresponding to the phosphorus atom [22].

The reactions of complexes **1**–**6** with KCN or KSCN in methanol solution show similar results. In both cases we observed the formation of a very insoluble white precipitate. The IR of the solids showed strong bands at 2116 and 2141 cm^{-1}, respectively, which correspond to the asymmetric stretching frequency of the CN group. These bands agreed with the values found in literature for the polymeric compounds $[(\eta^3\text{-Me-allyl})Pd(A)_x]_n$ $[A = CN^-, SCN^-]$ [23]. Moreover, the respective free ligands were recovered from the filtrate.

Finally, a complete decomposition of the complexes with NaH in acetonitrile solutions was observed. We detected the reduction of the metal to Pd°, a partial decomposition of the ligand and the formation of 3-methyl-1-propene.

These results indicate that the 2-(methylthio)-*N*-subtituted-benzylidene)anilines ligands bonded to the organometallic fragment $[(\eta^3\text{-Me-allyl})Pd]$ show that the thioether group of the Schiff base is not accessible for a cleavage of the C–S bond. In all cases the nucleophilic attack produced the deco-ordination of the Schiff base, and no demethylation reaction was observed. These results are different to those with complexes of the type $[Cl_2M(L_2)]$ (where M = Pd(II) or Pt(II) and L_2 is *o*-(diphenylphophino) thioanisole. In these cases the reaction with nucleophiles such as thiocynate, iodide or benzylamine, produces the cleavage of the C–S bond of the coordinated ligand transforming the methylthioether group into a thiolate group [3d,3e,3f].

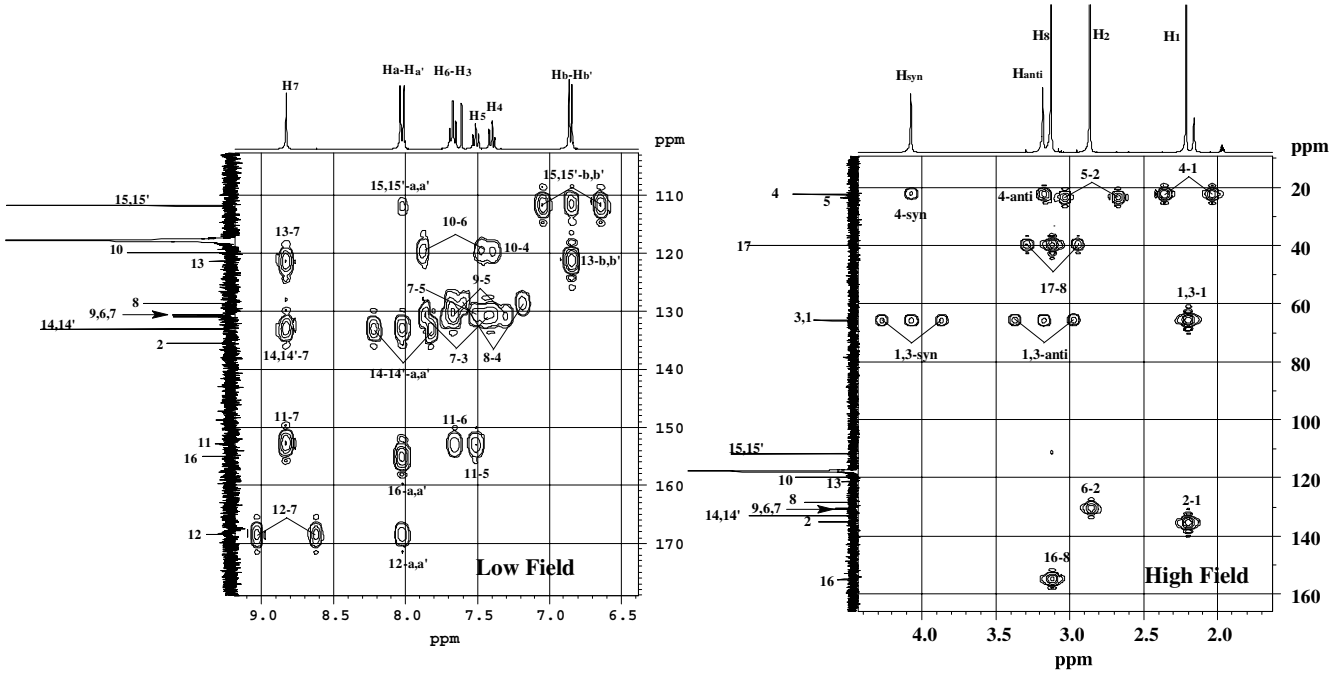
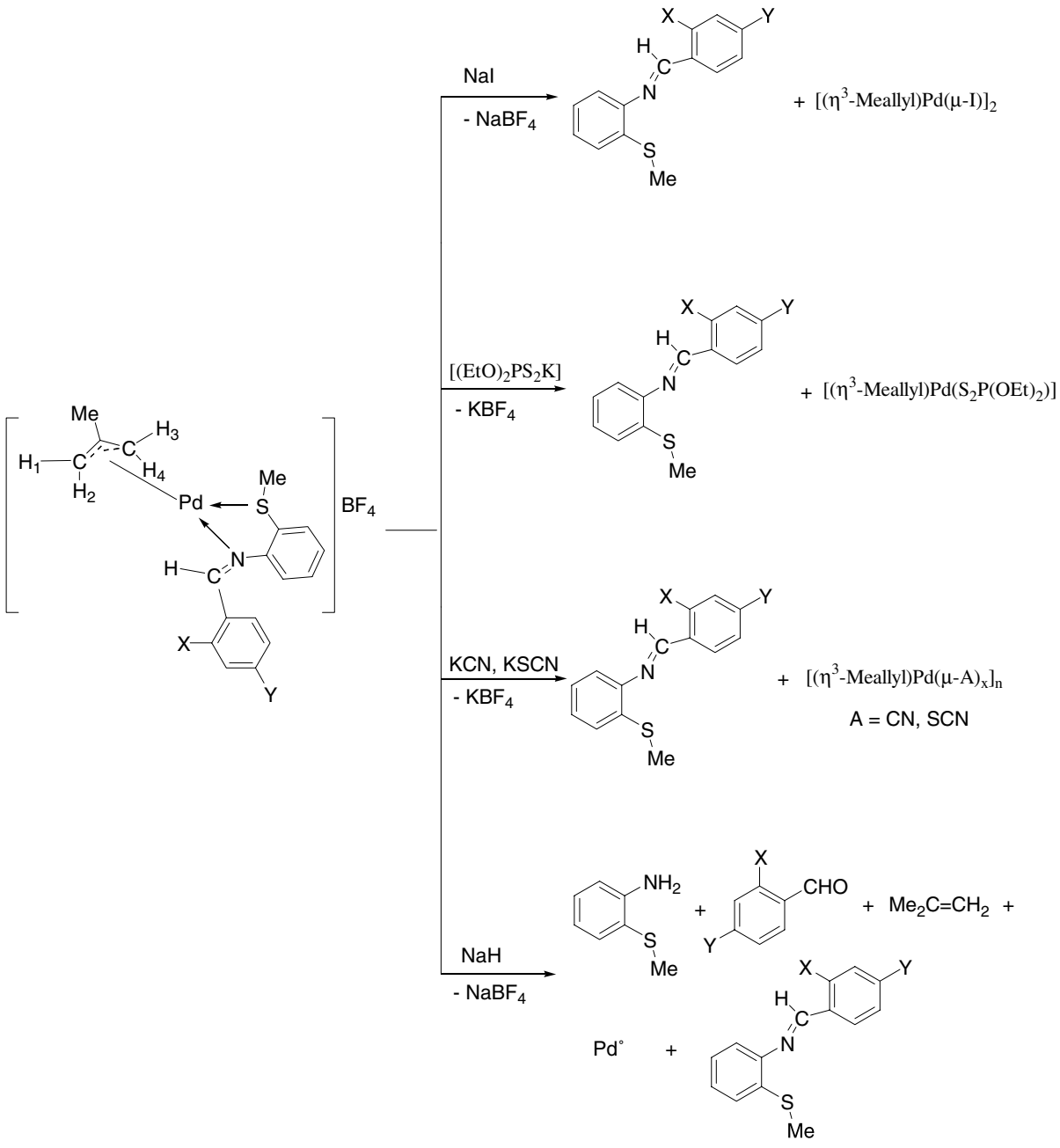


Fig. 2. ^1H–^{13}C COSY (HMBC) NMR spectrum of complex **5** in CD_3CN showing low and high field C–H correlation signals.



Scheme 3. Reactions of complexes **1**–**6** with nucleophiles.

Moreover, the attempts to exchange the bidentate ligand with a similar more basic ligand (i.e. reaction of complex **6** with the ligand $MeSC_6H_4N{=}CHC_6H_4NMe_2$) were unsuccessful. In all cases the ^1H NMR spectra show no variations respect to the starting complex. This experiment discards the possibility of the formation of a vacant site by deco-ordination of one end of the bidentate Schiff base ligand.

As a complement to the experimental reactivity reactions, theoretical calculations for complexes **1**, **5** and **6** were performed. The main goal was to explain the lack of reactivity of the Me–S group toward a nucleophilic attack. For this purpose a charge density analysis (natural charge analysis as defined in Gaussian 98 program) was performed. This was made for the atoms involved in the experimental target, i.e. the Me–S cleavage; the atoms that showed a high Fukui function toward a nucleophile, high $f(r)^+$, were also included. They corresponded to the iminic N and C atoms. The results obtained are summarised in Table 4. The three complexes show a very similar charge distribution for the selected atoms. Moreover, the S–C(Me) bond distances are also very close, and are slightly longer compared with these distances in the free ligand.

Table 4

Complex	Charge density (fukui function $f(r)^+$)				Bond distance (Å)	
	C_{12}	N	S	$Me(C_5)$	S–Me[a]	S–Me[b]
1	−0.2724 (0.339)	−0.2783 (0.214)	0.3028 (0.019)	−0.7773 (0.002)	1.8955	1.8829
5	−0.2937 (0.074)	−0.3018 (0.087)	0.3018 (0.122)	−0.7791 (0.011)	1.8951	1.8833
6	−0.2782 (0.159)	−0.2653 (0.152)	0.3041 (0.006)	−0.7767 (0.001)	1.8958	1.8829

[a] Complex.
[b] Free ligand.

A study of nucleophilic $f(r)^+$ and electrophilic $f(r)^-$ Fukui functions was performed. A graphical representation of the results for the $f(r)^+$ function of complexes **1**, **5** and **6** is displayed in Fig. 3.

It can be seen that the suitable sites for nucleophilic attack, $f(r)^+$, are located on the Pd center, the N atom and the C–H iminic bonds, while the S–Me moiety shows no electronic contribution in all complexes. Therefore, a nucleophile should attack the regions with high $f(r)^+$ function and not the S–Me bond, as would be expected in a demethylation reaction. Probably, in a first stage, the nucleophile attacks the iminic moiety or the metal center, and in a subsequent step the decoordination of the ligand takes place, yielding finally a polynuclear species.

On the basis of these results, and specially considering the fact that the Fukui functions do not present a distribution on the S–C(Me) fragment, the following can be concluded: (i) all three complexes should show a similar chemical reactivity toward nucleophilic attack, as observed in the experimental results; (ii) from a theoretical point of view, a nucleophilic attack should only occur on the metal or on the iminic moiety of the co-ordinated ligand; and (iii) in these systems, the S–C(Me) bond is not weak enough to transfer the methyl group to the incoming nucleophile.

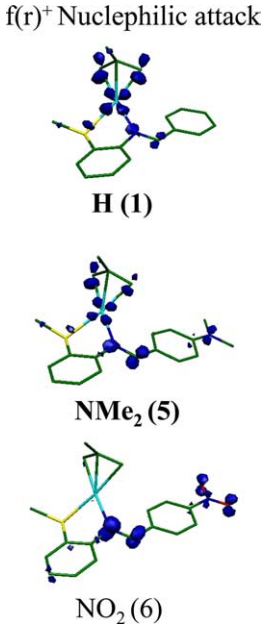


Fig. 3. Fukui function for complexes **1**, **5**, **6**.

The theoretical results analysed above are in agreement with the experimental behaviour, and support the reactivity routes proposed.

Acknowledgements

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References

[1] A. Bader, E. Lindner, Coord. Chem. Rev. 108 (1991) 27.
[2] (a) J. Albert, J. Granell, J. Mínguez, G. Muller, D. Sainz, P. Valerga, Organometallics 16 (1997) 3561;
(b) R. Contreras, M. Valderrama, C. Beroggi, D. Boys, Polyhedron 20 (2001) 3127;
(c) J. Dilworth, S. Howe, A. Hutson, J. Miller, J. Silver, R. Thompson, M. Harman, M. Hursthouse, J. Chem. Soc., Dalton Trans. (1994) 3553;
(d) G.K. Anderson, J. Organomet. Chem. 368 (1989) 385;
(e) M. Valderrama, R. Contreras, D. Boys, Polyhedron 16 (1997) 1811;
(f) A.L. Sanger, C.G. Lobe, J.E. Weiner-Fedorak, Inorg. Chim. Acta 53 (1981) L123;
(g) Y. Fuchita, Y. Ohta, K. Hiraki, M. Kawatani, N. Nishiyama, J. Chem. Soc., Dalton Trans. (1990) 3767;
(h) Y. Fuchita, K.J. Hardcastle, K. Hiraki, M. Kawatani, Bull. Chem. Soc. Jpn. 63 (1990) 1961;
(i) P. Romero, M. Valderrama, R. Contreras, D. Boys, J. Organomet. Chem. 673 (2003) 102.
[3] (a) J.S. Kim, J.H. Reibenspies, M.Y. Darensbourg, J. Am. Chem. Soc. 118 (1996) 4115;
(b) T.B. Rauchfuss, D.M. Roundhill, J. Am. Chem. Soc. 97 (1975) 3386;
(c) G. Dyer, M.O. Workman, D.W. Meek, Inorg. Chem. 6 (1967) 1404;
(d) D.M. Roundhill, W.B. Beaulieu, U. Bagchi, J. Am. Chem. Soc. 101 (1979) 5428;
(e) A. Benefiel, D.M. Roundhill, Inorg. Chem. 25 (1986) 4027;
(f) A. Benefiel, D.M. Roundhill, W.C. Fultz, A.L. Rheingold, Inorg. Chem. 23 (1984) 3316.
[4] F. Basuli, P. Chattopadhyay, C. Sinha, Polyhedron 15 (1995) 2439.

[5] (a) K. Selvakumar, S. Vancheesan, Polyhedron 15 (1996) 3979;
(b) K. Selvakumar, S. Vancheesan, Polyhedron 15 (1996) 2535;
(c) K. Selvakumar, S. Vancheesan, Polyhedron 14 (1995) 2091;
(d) P. Chattopadhyay, C. Sinha, Polyhedron 13 (1994) 2689.
[6] Spartan version 5.0 wave function, Inc. 18401 Von Karman Ave, No. 370 Irvine, CA 92715.
[7] (a) P. Parr, W. Yang, Density Functional of Atoms and Molecules, Oxford Press, New York, 1989;
(b) R. López, D. Boys, B. Loeb, F. Zuloaga, J. Chem. Soc., Perkin Trans. 2 (1998) 877.
[8] (a) R. Pearson, Chemical Hardness, Wiley–VCH, New York, 1997;
(b) R. Parr, W. Yang, J. Am. Chem. Soc. 106 (1984) 4049;
(c) K. Fukui, Acc. Chem. Res. 4 (1971) 57;
(d) R. Parr, P. Ayers, J. Am. Chem. Soc. 122 (2000) 2010.
[9] D.D. Perrin, W.L.F. Armarego, Purification of Laboratory Chemicals, third ed., 1988.
[10] K. Ding, Y. Wu, H. Hu, L. Shen, X. Wang, Organometallics 11 (1992) 3849.
[11] Y. Tatsuno, T. Yoshida, Y. Seiotsuka, Inorg. Synth. 19 (1970) 220.
[12] B.E. Mann, B.L. Shaw, G. Shaw, J. Chem. Soc. (A) (1971) 3536.
[13] R.G. Cavell, N. Byers, E.D. Day, Inorg. Chem. 10 (1971) 2710.
[14] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, A.G. Baboul, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, Gaussian 98, Revision A.7, Gaussian, Inc., Pittsburgh, PA, 1998.
[15] (a) A.D. Becke, Phys. Rev. A 38 (1988) 3098;
(b) A.D. Becke, J. Chem. Phys. 98 (1993) 1372;
(c) A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
[16] C. Lee, W. Yang, R. Parr, Phys. Rev. B 37 (1988) 785.
[17] P. Flukiger, H.P. Luthi, S. Portmann, J. Weber, MOLEKEL 4.1, Swiss Center for Scientific Computing, Manno (Switzerland), 2000–2001.
[18] (a) X. Almagro, W. Clegg, L. Cucurull-Sánchez, P. Gonzalez-Duarte, M. Traveria, J. Organomet. Chem. 623 (2001) 137;
(b) K. Selvakumar, S. Vancheesan, Polyhedron 16 (1997) 2405;
(c) A. Vetter, A. Berkessel, Synthesis (1995) 419.
[19] (a) J. Ruiz, J. Giner, V. Rodríguez, G. López, J. Casabó, E. Molins, C. Miravitlles, Polyhedron 19 (2000) 1627;
(b) J. Delis, J. Groen, K. Vrieze, P. Van Leeuwen, N. Veddman, A. Spek, Organometallics 16 (1997) 551;
(c) M. Grassi, S. Meille, A. Musco, R. Pontellini, A. Sironi, J. Chem. Soc., Dalton Trans (1990) 251;
(d) A. Albinati, P. Pregosin, F. Wombabacher, Inorg. Chem. 29 (1990) 1812.
[20] M.L. Creber, K.G. Orrell, A.G. Osborne, V. Sik, S.J. Coles, D.E. Hibbs, M.B. Hursthouse, Inorg. Chim. Acta 299 (2000) 209.
[21] D.M. Roundhill, S.G.N. Roundhill, W.B. Beaulieu, U. Bagchi, Inorg. Chem 19 (1980) 3365.
[22] R. Contreras, M. Valderrama, O. Riveros, R. Moscoso, D. Boys, Polyhedron 15 (1996) 183.
[23] B. Shaw, G. Shaw, J. Chem. Soc. (1971) 3533.