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Catalytic transformations of diazo compounds promoted by platinum(0) and dicationic platinum(II) complexes

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Abstract

9-Diazofluorene (DAF) is decomposed either stoichiometrically or catalytically in the presence of the platinum(0) complex $[Pt(C_2H_4)(PPh_3)_2]$ to give difluoren-9-ylidene-hydrazine in high yield. Under analogous reaction conditions, diphenyldiazomethane gives mostly the azine, $Ph_2C{=}N{-}N{=}CPh_2$, while ethyl diazoacetate (EDA) affords, in low yield, a mixture of diethyl fumarate and maleate in approximately 10:1 molar ratio. The cyclopropanation of styrene with EDA is catalyzed by a series of dicationic complexes of the type $[PtL_2(NCCH_3)_2][Y]_2$ ($L_2 = 2PPh_3$, $Ph_2PCH{=}CHPPh_2$, $Ph_2PCH_2CH_2PPh_2$; $Y = BF_4$, CF_3SO_3) in 1,2-dichloroethane at 60 °C for 24 h. DAF and EDA undergo insertion reactions into the O–H bond of alcohols ROH (R = Me, Et, *t*-Bu, $CH_2CH{=}CH_2$, Ph) at 25 °C in CH_2Cl_2–ROH (DAF or EDA–ROH molar ratio 1/20) in the presence of 1% mol of several dicationic platinum(II) complexes to give the corresponding ethers in excellent yields. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Platinum complexes; Diazo compounds; Carbenes; Insertion reactions; Cyclopropanation of olefins

1. Introduction

Diazo compounds of the general formula $N_2 = CRR'$ (R, R′ = H, alkyl, aryl) are versatile reagents in coordination as well as in synthetic organic chemistry since they can bind a metal center in a variety of modes or generate free or coordinated highly reactive carbene products in view of their propensity towards dinitrogen loss [1]. Among the variety of transformations of diazo compounds catalyzed by transition metal complexes that have been investigated such as the transfer of carbenes from diazo compounds to alkenes to give cyclopropanes and carbene insertions into polar X–H (X = N, O, S) bonds, those promoted by the rigid dirhodium(II) tetracarboxylates and the related dirhodium(II) carboxamidates have found a general applicability [1–3].

Platinum complexes, regardless of the oxidation state of the metal center (0, + 2, + 4), have also been shown to be active catalysts for the cyclopropanation of olefins with diazo compounds [4–6]. The involvement of a platinum(0) carbene species, e.g. $[Pt({=}CHCO_2Et)(PPh_3)_2]$ has been detected by fast-atom bombardment–mass spectrometry (FAB–MS) [5,7] in the reaction of $[Pt(C_2H_4)(PPh_3)_2]$ (**1**) with ethyl diazoacetate (EDA), N_2CHCO_2Et [8]. The insertion of carbenes into the O–H bond of alcohols catalyzed by neutral platinum(II) complexes provides the corresponding O–H insertion products in good yields [3].

No cationic platinum(II) complexes appear to have been investigated in the past as potential catalysts in the decomposition of diazo compounds, although these species are of interest due to both the enhancement of electrophilicity and the availability of readily accessible

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sites at the metal center [9]. These features have recently been explored [10] in the decomposition of 9-diazofluorene (DAF) to 9,9′-bifluorenylidene and the insertion of DAF-derived carbene into the O–H bond of MeOH to give 9-methoxyfluorene, both of which are catalyzed by *cis*-$[Pt(PPh_3)_2(CH_3CN)_2][BF_4]_2$ (**2**) (Scheme 1).

Preliminary results showed the dicationic complex **2** to be a highly efficient and chemospecific catalyst especially when compared with the neutral platinum(II) complex *cis*-$[PtCl_2(PPh_3)_2]$, which was inactive in these reactions, or with the dicationic rhodium(II) complex $[Rh_2(OAc)_2(CH_3CN)_6][BF_4]_2$ for which a complex mixture of products was obtained for the corresponding reaction of DAF in CH_2Cl_2–MeOH under the same reaction conditions employed for **2** [10].

Our interest in carbene chemistry [11] and the development of new catalytic systems for C–C and/or C–X bond forming reactions coupled with our interest in exploring the generality of the reaction chemistry illustrated in Scheme 1, led us to pursue the current work. We report herein the catalytic activity of the platinum(0) complex $[Pt(C_2H_4)(PPh_3)_2]$ (**1**) and that of the dicationic platinum(II) species of the general formula $[PtL_2(CH_3CN)_2][Y]_2$ ($L_2 = 2\ PPh_3$, $Ph_2PCH{=}CHPPh_2$, $Ph_2PCH_2CH_2PPh_2$; $Y = BF_4$, CF_3SO_3) and $[Pt_2(\mu\text{-}Cl)_2(PPh_3)_4][BF_4]_2$ towards some diazo compounds such as DAF, diphenyl diazomethane and EDA. In particular, catalytic transformations such as coupling of carbenes to give olefins, cyclopropanation of styrene and insertion reactions of carbenes into the O–H bond of alcohols will be reported. These results will be compared with those obtained with neutral platinum(II) complexes of the type $[PtCl_2L_2]$.

2. Experimental

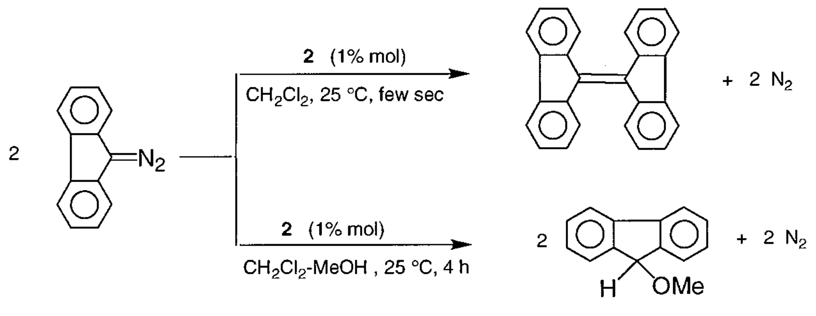
2.1. General procedures and materials

All work was carried out with the exclusion of atmospheric oxygen under a dinitrogen atmosphere using standard Schlenck techniques. Unless otherwise stated, solvents were used as received; CH_2Cl_2 and toluene were distilled over CaH_2, diethylether and THF were distilled over sodium benzophenone. Infrared (IR) spectra were recorded on a Perkin–Elmer 983 spectrophotometer. ^1H-, $^{31}P\{^1H\}$- and $^{13}C\{^1H\}$-NMR spectra were run on a Bruker AC-200 spectrometer operating at 200.13, 81.015 and 50.32 MHz, respectively. Peak positions are reported relative to Me_4Si and were calibrated against the residual solvent resonance (^1H) or the deuterated solvent multiplet (^{13}C). The ^{31}P-NMR spectra were referenced against external H_3PO_4 85%. Gas chromatography–mass spectrometry (GC–MS) data were obtained with a QMD 1000 Carlo Erba instrument, using a PS 264 30 m column, with a He flux of 1 ml min^{-1}, temperature range of 150 °C (100–250 °C) with a gradient of 10 °C min^{-1}. Mass spectrometric measurements were performed on triple-quadrupole (VG Quattro, VG Fisons, Altrinchan, UK) and ZAB 2F (VG) instruments [12] equipped with FAB sources, bombarding 3-nitrobenzylalcohol (Aldrich 98%) solutions of the samples [13].

The compounds $[Pt(C_2H_4)(PPh_3)_2]$ (**1**) [14], *cis*-$[PtCl_2(PPh_3)_2]$ [15], $[PtCl_2(Ph_2PCH_2CH_2PPh_2)]$ [16], $[PtCl_2(Ph_2PCH{=}CHPPh_2)]$ [16], $[Pt_2(\mu\text{-}Cl)_2(PPh_3)_4][BF_4]_2$ [11], $[Pt(PPh_3)_2(CH_3CN)_2][BF_4]_2$ (**2**) [10], DAF [17] and diphenyl diazomethane [18,19] were prepared as described in the literature. EDA was purchased from Aldrich and was used as received. The stability of DAF towards decomposition at 25 °C over 24 h was tested by ^1H-NMR spectroscopy. DAF (1.90 mg, 1.0×10^{-2} mmol) was dissolved in a nuclear magnetic resonance (NMR) tube using either $CDCl_3$ (1 ml) or CD_3CN (1 ml) and the corresponding NMR spectra were recorded at regular time intervals. After 24 h, a partial thermal decomposition of DAF is observed with the formation of difluoren-9-hydrazine and 9,9′-bifluorenylidene (ca. 20 and $< 10\%$ in $CDCl_3$ and ca. 10 and $< 5\%$ in CD_3CN, respectively).

2.2. Synthesis of cis-$[Pt(PPh_3)_2(CH_3CN)_2][CF_3SO_3]_2$ (3)

The synthesis of **3** is similar to that previously reported for **2** [10]. A suspension of *cis*-$[PtCl_2(PPh_3)_2]$



Scheme 1.

(500 mg, 0.63 mmol) in CH_2Cl_2 (15 ml) and CH_3CN (5 ml) at 0 °C was treated with $AgCF_3SO_3$ (3.25 ml of a 0.389 M acetone solution, 1.265 mmol). The reaction mixture was stirred for 3 h and then the solid AgCl that formed was removed by filtration. The solution was concentrated to a small volume and then Et_2O was added until a white solid precipitate, which was filtered off and dried under vacuum. Yield 492 mg (71%). IR (Nujol mull): $\nu_{C\equiv N} = 2306$, 2324, 2337 cm^{-1}. $^{31}P\{^1H\}$-NMR (CD_3CN): δ 3.74 (s, $^1J_{PtP}$ 3689 Hz). $^{31}P\{^1H\}$-NMR (CD_2Cl_2): δ 8.00 (s, $^1J_{PtP}$ 3718 Hz), 5.82 (s, $^1J_{PtP}$ 4104 Hz) with a ca. 1:1 integratio ratio. The two signals can be tentatively explained with the presence in CD_2Cl_2 of two species i.e. *cis*-$[Pt(PPh_3)_2(CH_3CN)_2][CF_3SO_3]_2$ and *cis*-$[Pt(PPh_3)_2(CF_3SO_3)_2]$.

2.3. Synthesis of $[Pt(Ph_2PCH{=}CHPPh_2)(CH_3CN)_2][CF_3SO_3]_2$ (4)

The synthesis of **4** is similar to that reported for **3** starting from *cis*-$[PtCl_2(Ph_2PCH{=}CHPPh_2)]$ (125 mg, 0.188 mmol) and $AgCF_3SO_3$ (0.97 ml of a 0.389 M acetone solution, 0.377 mmol). Yield 135 mg (75%). IR (Nujol mull): $\nu_{C\equiv N} = 2300$, 2325 cm^{-1}. $^{31}P\{^1H\}$-NMR (CD_3CN): δ 47.7 (s, $^1J_{PtP}$ 3657 Hz).

2.4. Synthesis of $[Pt(Ph_2PCH_2CH_2PPh_2)(CH_3CN)_2][CF_3SO_3]_2$ (5)

The synthesis of **5** is similar to that reported for **3** starting from *cis*-$[PtCl_2(Ph_2PCH{=}CHPPh_2)]$ (125 mg, 0.188 mmol) and $AgCF_3SO_3$ (0.97 ml of a 0.389 M acetone solution, 0.376 mmol). Yield 132 mg (72%). IR (Nujol mull): $\nu_{C\equiv N} = 2300$, 2320 cm^{-1}. $^{31}P\{^1H\}$-NMR (CD_3CN): δ 41.8 (s, $^1J_{PtP}$ 3586 Hz).

2.5. Synthesis of $[Pt_2(\mu\text{-}Cl)_2(PPh_3)_4][BF_4]_2$ (6)

To a suspension of *cis*-$[PtCl_2(PPh_3)_2]$ (790 mg, 1.00 mmol) in CH_2Cl_2 (15 ml) was added $AgBF_4$ (1.5 ml of a 0.65 M acetone solution, 1.00 mmol) at room temperature (r.t.). The reaction mixture was stirred for 30 min and then the solid AgCl formed was removed by filtration. The solution was reduced to low volume and treated with Et_2O to give a white solid, which was filtered off and dried under vacuum. Yield 750 mg (89%). $^{31}P\{1H\}$-NMR ($CDCl_3$): δ 14.6 (s, $^1J_{PtP}$ 3855 Hz). $^{31}P\{^1H\}$-NMR (CD_3CN): δ 13.3 (d, $^1J_{PtP}$ 3506 Hz, $^2J_{PP}$ 18.6 Hz), 5.75 (d, $^1J_{PtP}$ 3832 Hz, $^2J_{PP}$ 18.6 Hz).

2.6. Decomposition of diazo compounds promoted by 1

2.6.1. Diazofluorene (DAF)

The reaction of DAF in the presence of **1** was carried out either stoichiometrically or catalytically. In the stoichiometric reaction, complex **1** (200 mg, 0.267 mmol) dissolved in CH_2Cl_2 (50 ml) was stirred with DAF (103 mg, 0.534 mmol) at r.t. for 12 h. During the time of reaction, the color changed from orange to deep red. The course of the reaction was followed by IR spectroscopy by observing the disappearance of the N≡N band of DAF at 2085 cm^{-1} and the appearance of a new C=N band at 1623 cm^{-1}. The red precipitate that formed was filtered off and dried under vacuum. Yield 87 mg (92%). Anal. Calc. for $C_{26}H_{16}N_2$: C, 87.61; H, 4.52; N, 7.86. Found: C, 87.61; H, 4.52; N, 7.86%. IR (Nujol mull): $\nu_{C=N} = 1623$ cm^{-1}. ^1H-NMR ($CDCl_3$): δ 7.24–7.55 (8H, m), 7.67–7.71 (4H, m), 8.07–8.20 (4H, m). The mother liquors were concentrated to a small volume and *n*-hexane was added to give a white solid, which was filtered off and dried under vacuum. The product was identified on the basis of microanalytical data and its $^{31}P\{^1H\}$-NMR as the known [20] platinum(II) complex $[Pt(PPh_3)_2(CO_3)]$. Yield 170 mg (81%). Anal. Calc. for $C_{37}H_{30}P_2O_3Pt$: C, 57.00; H, 3.88. Found: C, 55.45; H, 3.86%. $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 6.55 (s, $^1J_{PtP}$ 3705 Hz).

The catalytic test was performed as follows. In a two-neck round bottom flask with an inlet/outlet for N_2 were introduced **1** (23.4 mg, 3.13×10^{-2} mmol) and DAF (602 mg, 3.13 mmol) in 1,2-dichloroethane (50 ml). The reaction system was thermostated at 50 °C and stirred for 8 h. After this time, an IR spectrum showed the complete disappearance of the N≡N band of DAF. The reaction mixture was then concentrated to a small volume (3 ml). The red solid formed was filtered off and identified by ^1H-NMR as difluoren-9-ylidene hydrazine. In an analogous experiment, after the first 8 h, a further 3.13 mmol of DAF were added to the reaction mixture. Once again, DAF was consumed after 8 h. These experiments were repeated several times with no evidence of loss of catalytic activity by **1**.

2.6.2. Diphenyl diazomethane

The reaction of $Ph_2C{=}N_2$ in the presence of **1** was carried out stoichiometrically. Complex **1** (150 mg, 0.20 mmol) dissolved in CH_2Cl_2 (40 ml) was mixed with $Ph_2C{=}N_2$ (77 mg, 0.40 mmol) at r.t. The reaction was followed by IR spectroscopy observing the disappearance of the N≡N band of $Ph_2C{=}N_2$ at 2047 cm^{-1} and the appearance of a new C=N band at 1619 cm^{-1}. After 3 days, the N≡N band had completely disappeared. ^1H-NMR data [21] of the reaction mixture showed that the azine $Ph_2C{=}N{-}N{=}CPh_2$ was formed as the major product together with a small amount ($<$ 10%) of the olefin $Ph_2C{=}CPh_2$. The mother liquors were concentrated to a small volume and *n*-hexane was added to give a white solid, which was filtered off and dried under vacuum. The product was identified [20] as $[Pt(PPh_3)_2(CO_3)]$. Yield 132 mg (85%).

2.6.3. Diethyl diazoacetate (EDA)

The stoichiometric reaction of EDA in the presence of **1** was performed as described previously [8]. The catalytic test was performed as described for DAF starting from **1** (21.3 mg, 2.85×10^{-2} mmol) and EDA (0.3 ml, 2.85 mmol) in 1,2-dichloroethane (50 ml) at 50 °C for 8 h. After this time, the IR spectrum of the reaction mixture showed a strong N≡N band of EDA at 2109 cm^{-1}. The reaction mixture was analyzed by GC–MS showing the presence of a small amount of a mixture of diethyl fumarate and diethyl maleate in a ca. 10:1 ratio. The solvent was removed to give a whitish residue, which was mostly $Ph_3P{=}O$ as revealed by ^{31}P-NMR.

2.7. Cyclopropanation of styrene catalyzed by dicationic platinum(II) complexes

All of the cyclopropanation reactions were carried out under analogous experimental conditions to those described herein. In a three-necked round bottom flask equipped with an inlet/outlet for N_2 and dropping funnel were placed the catalyst (1.025×10^{-2} mmol) and styrene (1.2 ml, 10.25 mmol) dissolved in 1,2-dichloroethane (10 ml), and the reaction system was thermostated at 60 °C. A solution of EDA (0.11 ml, 1.025 mmol) in 1,2-dichloroethane (2 ml) was added dropwise over a 4 h period. After this time, the reaction mixture was stirred for an additional 20 h at the same temperature and then it was analyzed by GC–MS. The pure reference samples of *cis*- and *trans*-2-phenylcyclopropane ethylcarboxylates have been prepared starting from the corresponding acids [22].

2.8. Insertion of carbenes derived from DAF into the O–H bond of alcohols ROH catalyzed by dicationic platinum(II) complexes

All of the insertion reactions were carried out under analogous experimental conditions as those described herein. In a three-necked round bottom flask equipped with an inlet/outlet for N_2 and dropping funnel were placed the catalyst **2**, **3** or **6** (1.0×10^{-2} mmol) and the alcohol ROH (20 mmol) in CH_2Cl_2 (5 ml) and the reaction system was thermostated at 25 °C. A solution of DAF (197 mg, 1.0 mmol) dissolved in CH_2Cl_2 (10 ml) was added dropwise over a 4 h period. After this time, the reaction mixture was stirred until the N≡N band of the starting diazo compound at 2085 cm^{-1} was no longer observed in the IR spectrum (ca. 0.5–2 h depending on the alcohol employed). The solution was then reduced to a small volume, treated with Et_2O to remove the catalyst and then taken to dryness to give a solid residue of the insertion product. The compound 9-methoxyfluorene, derived from the reaction with MeOH, has been reported previously [10]. Data for the other compounds are given below.

2.8.1. 9-Ethoxyfluorene

Yield 192 mg (92%). ^{1}H-NMR ($CDCl_3$): δ 1.16 (t, $^3J_{HH}$ 7.0, 3H, CH_3), 3.27 (q, 2H, OCH_2), 5.63 (s, 1H, CH), 7.26–7.69 (m, aromatic protons). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 14.98 (s, CH_3), 61.07 (s, OCH_2), 81.48 (s, CH), 120.5–143.8 (aromatic carbons). GC–MS (retention time 16.03 min): *m*/*z* 210 ($[M]^+$, 60%), 181 ($[M - {}^{\bullet}C_2H_5]^{+\bullet}$, 100%), 165 ($[M - {}^{\bullet}OC_2H_5]^{+\bullet}$, 90%), 152 ($[C_6H_8]^+$, 45%).

2.8.2. 9-Tert-butoxyfluorene

Yield 183 mg (77%). ^{1}H-NMR ($CDCl_3$): δ 1.54 (s, 12H, CH_3), 5.56 (s, 1H, CH), 7.26–7.86 (m, aromatic protons). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 30.13 (s, CH_3), 75.7 (s, CH), 74.8 (s, $C(CH_3)_3$), 123.4–146.5 (aromatic carbons). GC–MS (retention time 20.25 min): *m*/*z* 238 ($[M]^+$, 10%), 181 ($[M - {}^{\bullet}C_4H_9]^{+\bullet}$, 100%), 165 ($[M - {}^{\bullet}OC_4H_9]^{+\bullet}$, 80%), 152 ($[C_6H_8]^+$, 30%).

2.8.3. 9-Allyloxyfluorene

Yield 190 mg (86%). ^{1}H-NMR ($CDCl_3$): δ 3.69–3.73 (m, 2H, OCH_2), 5.10–5.30 (m, 2H, CH_2), 5.69 (s, 1H, CH), 5.82–5.96 (m, 1H, $CH_{allylic}$), 7.26–7.70 (m, aromatic protons). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 66.51 (s, $CH_2{=}CHCH_2$), 81.24 (s, CHO), 117.3 (s, $CH_2{=}CHCH_2$), 135.7 (s, $CH_2{=}CHCH_2$), 120.5–143.5 (aromatic carbons). GC–MS (retention time 17.18 min): *m*/*z* 222 ($[M]^+$, 10%), 181 ($[M - {}^{\bullet}C_3H_5]^{+\bullet}$, 100%), 165 ($[M - {}^{\bullet}OC_3H_5]^{+\bullet}$, 85%), 152 ($[C_6H_8]^+$, 30%).

2.8.4. 9-Phenoxyfluorene

Yield 240 mg (93%). ^{1}H-NMR ($CDCl_3$): δ 5.00 (s, 1H, CH), 6.71–7.16 (aromatic protons of phenol), 7.26–7.69 (m, aromatic protons of fluorene). GC–MS (retention time 19.75 min): *m*/*z* 258 ($[M]^+$, 100%). A partial decomposition (ca. 7%) to the olefin 9,9′-bifluorenylidene was observed in this reaction.

2.9. Insertion of carbenes derived from EDA into the O–H bond of alcohols ROH catalyzed by dicationic platinum(II) complexes

The insertion reactions were carried out as described for the reactions of DAF in Section 2.8.

2.9.1. Methoxy-acetic acid ethyl ester

^{1}H-NMR ($CDCl_3$): δ 1.24 (t, $^3J_{HH}$ 7.2, 3H, CH_3), 3.37 (s, 3H, OCH_3), 3.97 (s, 2H, OCH_2), 4.16 (q, $^3J_{HH}$ 7.2, 2H, CH_2). GC–MS (retention time 2.7 min): *m*/*z* 89 ($[M - {}^{\bullet}C_2H_5]^{+\bullet}$, 40%), 45 ($[C_2H_5O]^+$, 100%).

2.9.2. Ethoxy-acetic acid ethyl ester

^{1}H-NMR ($CDCl_3$): δ 1.16 (t, $^3J_{HH}$ 7.0, 3H, CH_3), 1.23 (t, $^3J_{HH}$ 7.1, 3H, CH_3), 3.54 (q, $^3J_{HH}$ 7.0, 2H, CH_2), 4.16 (q, $^3J_{HH}$ 7.1, 2H, CH_2), 5.02 (s, 2H, OCH_2). GC–MS (retention time 3.3 min): *m*/*z* 103 ($[M - {}^{\bullet}C_2H_5]^{+\bullet}$, 3%), 88 ($[M - {}^{\bullet}C_2H_4O]^{+\bullet}$, 40%), 59 ($[C_3H_7O]^{+}$, 100%).

2.9.3. Allyloxy-acetic acid ethyl ester

^{1}H-NMR ($CDCl_3$): δ 1.25 (t, $^3J_{HH}$ 7.1, 3H, CH_3), 4.04 (s, 2H, OCH_2), 4.05 (m, 2H, OCH_2), 4.19 (q, $^3J_{HH}$ 7.1, 2H, CH_2), 5.16–5.31 (m, 2H, CH_2=), 5.82–5.95 (m, 1H, CH=). GC–MS (retention time 4.78 min): *m*/*z* 88 ($[M - C_3H_6]^{+\bullet}$, 40%), 41 ($[C_3H_5]^{+}$, 100%).

2.9.4. tert-Buthoxy-acetic acid ethyl ester

^{1}H-NMR ($CDCl_3$): δ 1.19 (s, 9H, CH_3), 1.23 (t, $^3J_{HH}$ 7.1, 3H, CH_3), 3.97 (s, 2H, OCH_2), 4.16 (q, $^3J_{HH}$ 7.1, 2H, CH_2). GC–MS (retention time 5.22 min): *m*/*z* 145 ($[M - {}^{\bullet}CH_3]^{+\bullet}$, 35%), 87 ($[C_5H_{11}O]^{+}$, 20%), 57 ($[C_4H_9]^{+}$, 100%).

2.9.5. Phenoxy-acetic acid ethyl ester

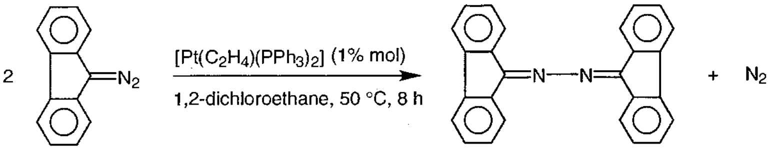
^{1}H-NMR ($CDCl_3$): δ 1.23 (t, $^3J_{HH}$ 7.1, 3H, CH_3), 4.90 (s, 2H, OCH_2), 4.16 (q, $^3J_{HH}$ 7.1, 2H, CH_2), 6.77–7.15 (aromatic protons of phenol). GC–MS (retention time 7.62 min): *m*/*z* 122 ($[C_7H_6O_2]^{+}$, 90%), 105 ($[C_7H_5O]^{+}$, 100%), 77 ($[C_6H_5]^{+}$, 80%).

3. Results and discussion

3.1. Decomposition of diazo compounds catalyzed by platinum(0) complexes

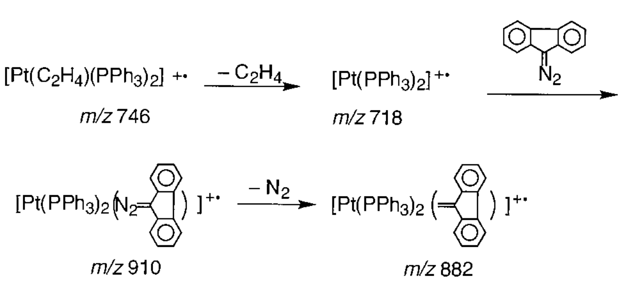
3.1.1. Reactions of 9-diazofluorene (DAF)

DAF is catalytically decomposed by $[Pt(C_2H_4)(PPh_3)_2]$ (**1**) (1% mol) to give difluoren-9-ylidene hydrazine in 80% yield when stirred in 1,2-dichloroethane at 50 °C for 8 h (Eq. (1)).



(1)

After this time, the metal catalyst is still active as confirmed by the conversion to the azine of a further amount of DAF under the same experimental conditions (see Section 2). Reaction (1) also proceeds stoichiometrically (complex/DAF in a 1/2 molar ratio) in CH_2Cl_2 at r.t. in 12 h to give difluoren-9-ylidene hydrazine in 92% yield. The azine was the only product isolated and was identified by ^{1}H-NMR and IR spectroscopy and microanalysis. No reaction intermediates were detected upon following reaction (1) by ^{1}H- and ^{31}P-NMR; by IR spectroscopy, the disappearance of the N≡N band at 2085 cm^{-1} of the starting diazo compound is accompanied by the formation of the C=N absorption band of the final product at 1623 cm^{-1}. Work up in air of the reaction mixture in the case of the stoichiometric reaction led to the isolation of the known [20] platinum(II) complex $[Pt(PPh_3)_2(CO_3)]$, likely formed [20] from the reaction of the $\{Pt(PPh_3)_2\}$ species with O_2 and CO_2.



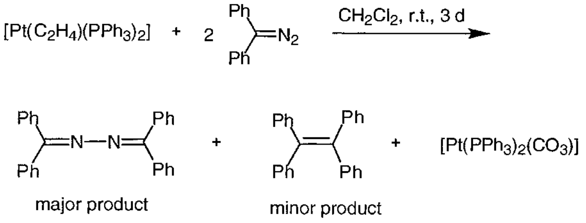
Scheme 2.

The FAB mass spectrum obtained after mixing (**1**) and DAF in a 1:5 molar ratio in a nitrobenzyl alcohol matrix showed the presence of ionic species (Scheme 2) that are likely to be involved in reaction (1) also in analogy with previous investigations of these reactions [5,7].

The loss of ethylene from the ionic species $[Pt(C_2H_4)(PPh_3)_2]^{+\bullet}$ (*m*/*z* 746) gives the species $[Pt(PPh_3)_2]^{+\bullet}$ (*m*/*z* 718) which may coordinate one molecule of DAF to give the adduct at *m*/*z* 910. Subsequent loss of N_2 from this latter species gives the carbene intermediate at *m*/*z* 882. No other species with higher molecular weight such as the olefin, 9,9′-bifluorenylidene, that might be formed upon carbene dimerization or the azine, either free or metal coordinated, were detected, possibly due to the fact that the formation of the olefin or the azine is slow on the mass spectrum time scale. It is interesting to note that the formation of azine in reaction (1) is not the product of the thermal decomposition of DAF (being 9,9′-bifluorenylidene). The olefin was the only product observed in the catalytic decomposition of DAF by the dicationic platinum(II) complex *cis*-$[Pt(PPh_3)_2(CH_3CN)_2][BF_4]_2$ [10].

3.1.2. Reaction of diphenyl diazomethane

The reaction of **1** with diphenyl diazomethane was performed stoichiometrically in a 1:2 molar ratio in CH_2Cl_2 at r.t. over 3 days to give the diphenyl ylidene hydrazine as the major product (Eq. (2)).

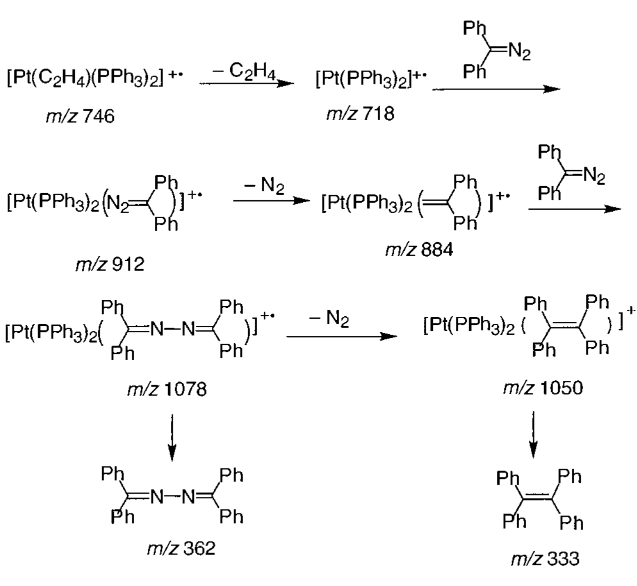


(2)

Also in this case, work up of the reaction mixture gave the platinum(II) carbonato complex. It is worth noting that reaction (2) carried out in the absence of complex **1** under the same experimental conditions was not complete after 6 days, as evidenced by the IR spectrum, which showed the presence of residual strong ν(N≡N) stretching of the diazo compound at 2045 cm^{-1} together with the ν(C=N) stretching at 1619 cm^{-1} of the corresponding azine.

The FAB mass spectrum obtained after mixing **1** and $Ph_2C{=}N_2$ in a 1:5 molar ratio in a nitrobenzyl alcohol matrix showed the presence of ionic species (Scheme 3) that may be involved in the reaction.

The corresponding FAB–MS reaction of DAF (Scheme 2), the initial loss of ethylene gives rise to $[Pt(PPh_3)_2]^{+\bullet}$ which coordinates a molecule of diphenyl diazomethane to form the adduct at *m*/*z* 912 as observed for the corresponding reaction of DAF (Scheme 2). From these latter species, loss of N_2 affords the well evident carbene intermediate at *m*/*z* 884, which then reacts with a second molecule of diphenyl diazomethane to yield the ionic species at *m*/*z* 1078 corresponding to the azine complex. These latter ionic species can decompose either forming the metal-free azine (shown to be the main reaction pathway) or to afford the olefin complex at *m*/*z* 1050, which then decomposes to give the free olefin.

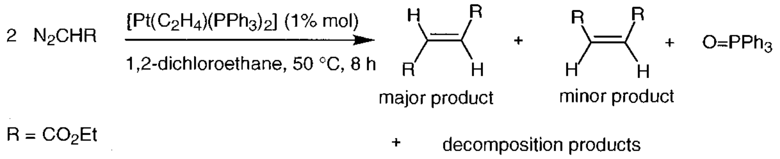


Scheme 3.

The results shown in Schemes 2 and 3 may be compared with those reported for the analogous reactions in the presence of the Au(I) complex $[Au(C_6F_5)(SC_4H_8)]$ [21], which reacts with $Ph_2C{=}N_2$ forming the corresponding azine complex, promoting N_2 elimination from DAF to give the corresponding free olefin.

3.1.3. Reactions of ethyl diazoacetate

The stoichiometric reaction of EDA with **1** has been obtained previously [8] affording the platinum fumarate complex $[Pt(PPh_3)_2($*trans*-$CO_2EtCH{=}CHCO_2Et)]$ as the only product with no evidence for the formation of either the maleate derivative or the azine. This reaction was studied by FAB mass spectrometry [5,7], which showed a reaction pathway similar to those reported in Schemes 2 and 3 for DAF and $Ph_2C{=}N_2$, respectively. The corresponding catalytic reaction (Eq. (3)) does not proceed to a significant extent presumably owing to the initial formation of the fumarate complex, which decomposes under the experimental conditions. The formation of the mixture of diethyl fumarate and maleate (in a ca. 10% yield with 10:1 ratio) can be rationalized as a thermal decomposition of the diazo compound.



(3)

3.2. Cyclopropanation of styrene catalyzed by dicationic platinum(II) complexes

The dicationic complexes $[PtL_2(CH_3CN)_2][Y]_2$ ($Y =$ BF_4, CF_3SO_3) were prepared starting from the corresponding chloro derivatives by reaction with two equivalents of AgY as reported in Eq. (4):

$$[PtL_2Cl_2] \xrightarrow[CH_2Cl_2/CH_3CN,\ RT,\ 1\ h]{+\,2AgY,\ -\,2AgCl} [PtL_2(CH_3CN)_2][Y]_2$$

$L_2 = 2\ PPh_3$, $Y = BF_4$ **(2)**
$L_2 = 2\ PPh_3$, $Y = CF_3SO_3$ **(3)**
$L_2 = Ph_2PCH{=}CHPPh_2$, $Y = CF_3SO_3$ **(4)**
$L_2 = Ph_2PCH_2CH_2PPh_2$, $Y = CF_3SO_3$ **(5)**

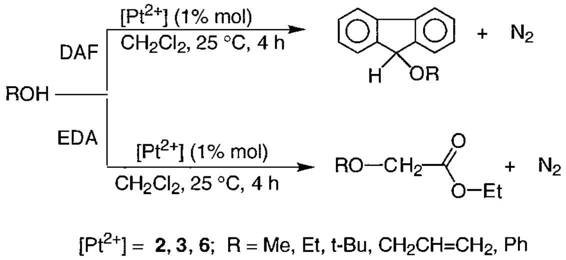
(4)

Compounds **2**–**5** were characterized by ^1H- and $^{31}P\{^1H\}$-NMR (see Section 2). The dicationic complexes **2**–**5** proved to be active catalysts in the cyclopropanation of styrene (Eq. (5)). The synthesis of cyclopropanes was performed by the dropwise addition (4 h) of a solution of EDA in 1,2-dichloroethane to a solution of the catalyst (1% mol) and styrene (styrene–EDA 10/1 molar ratio) in 1,2-dichloroethane at 60 °C. After the addition was complete, the reaction mixture was stirred for an additional 20 h at 60 °C.

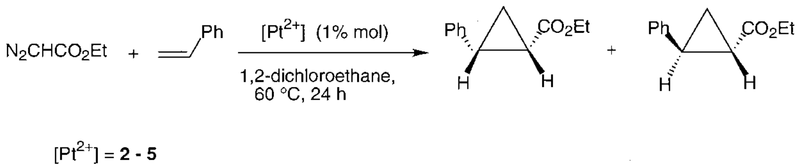
Table 1
Cyclopropanation of styrene with EDA in the presence of dicationic platinum(II) complexes [a]

Catalyst	Cyclopropanation yield (%)	*Cis*/*trans* ratio [b]
2	46	0.54
3	34	0.52
4	55 [c]	0.51
5	47	0.50

[a] Reaction conditions reported in the Section 2.
[b] Based on EDA and determined by GLC analysis.
[c] The yield was 90% after a reaction time of 48 h at 60 °C.



Scheme 4.



(5)

In all cases a mixture of *cis*- and *trans*-cyclopropane esters is formed, with the latter isomers being the major reaction products of the reactions (Table 1). In fact, the *cis*/*trans* ratio ranged from 0.50 to 0.54, with only very small variations among the different Pt(II) catalysts employed, thus indicating a negligible influence of both types of P-ligands coordinated to the metal center and the counter ion (BF_4 or CF_3SO_3). However, the reactions reported in Eq. (2) proceed in a very selective manner since the cyclopropane esters were the only products isolated with no evidence of the formation of side products such as the carbene dimers diethyl fumarate and diethyl maleate.

The results obtained for the dicationic platinum(II) complexes reported in this study may be compared with those reported by Demonceau et al. using platinum(0), neutral platinum(II) and platinum(IV) complexes [6]. At 60 °C (catalyst, 0.0025 mmol; styrene, 20 mmol; EDA, 1 mmol), the cyclopropanation yield and the *cis*/*trans* ratio of the cyclopropane isomers were found in the range of 34–79 and 0.60–0.65% (except for $PtCl_4$, which was 0.72), respectively.

3.3. Insertion of carbenes into the O–H bond of alcohols

The dicationic complexes **2**, **3** and the dinuclear chloro-bridged complex $[Pt_2(\mu\text{-}Cl)_2(PPh_3)_4][BF_4]_2$ (**6**), which was obtained by reaction of *cis*-$[PtCl_2(PPh_3)_2]$ with one equivalent of $AgBF_4$ (see Section 2), proved to be highly active catalysts in the insertion reactions of DAF- and EDA-derived carbenes into the O–H bond of alcohols to give the corresponding ethers in almost quantitative yield (Scheme 4).

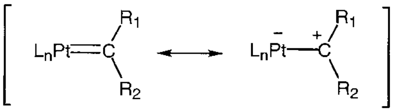
The reactions were carried out at 25 °C by dropwise addition (4 h) of a solution of EDA in dichloromethane to a solution in CH_2Cl_2 of the catalyst (1% mol) and the alcohol (DAF or EDA/ROH 1/20 molar ratio). The reactions were followed by IR spectroscopy observing the disappearance of the N≡N stretching of the diazo compound, which occurred after ca. 30–120 min after the addition was complete. The reactions were highly chemospecific since the ether derivatives were the only observed reaction products. Thus, no coupling of carbenes to give the corresponding olefins or azines was detected. Furthermore, in the case of the reaction of allylic alcohol, only one of the two possible products was formed i.e. the product resulting from the insertion into the O–H bond of the alcohol and not that resulting from the addition of the diazo-derived carbene to the double bond to give a cyclopropane.

It must also be noted that the insertion reactions reported in Scheme 4 do not proceed under analogous experimental conditions with the neutral platinum(II) complex *cis*-$[PtCl_2(PPh_3)_2]$ or with the platinum(0) species $[Pt(C_2H_4)(PPh_3)_2]$ and as a general feature, the dicationic platinum(II) complexes show a higher catalytic activity as compared with other neutral platinum(II) and platinum(IV) complexes reported previously [3].

4. Conclusions

We have described in this study the catalytic activity of some platinum(0) and dicationic platinum(II) complexes towards the decomposition of diazo compounds such as DAF, diphenyl diazomethane and ethyl diazoacetate. In some cases, the reactivity of the catalyst is influenced by the metal oxidation state and the type of diazo compound employed. Thus, for instance, while catalytic decomposition of DAF by $[Pt(C_2H_4)(PPh_3)_2]$ (**1**) gives rise selectively to the corresponding azine, the dicationic complex *cis*-$[Pt(PPh_3)_2(CH_3CN)_2][BF_4]_2$ (**2**) was previously reported to catalyze the formation of the corresponding olefin [10]. The dicationic complexes have been shown to be efficient catalysts in the cyclopropanation of styrene with EDA and in the insertion of carbenes derived either from DAF or EDA in the O–H bond of alcohols to give ethers. These latter reactions generally proceed under milder conditions and with higher yields than those reported for platinum(II) complexes [3]. As a matter of fact, using DAF as the carbene precursor and the neutral complex *cis*-$[PtCl_2(PPh_3)_2]$ we did not observe any insertion into the O–H bond of MeOH.

All the reactions reported in this work presumably occur through the intermediacy of a platinum–carbene species derived by initial interaction of the diazo compound with the metal substrate, followed by dinitrogen loss as demonstrated by fast atom bombardment mass spectrometric studies [5,7].



It should be noted that the electrophilicity of the carbene carbon will most likely be enhanced for the cationic platinum(II) species as compared with neutral complexes and this would explain their general higher reactivity compared to the corresponding neutral complexes in the insertion of carbenes into the O–H bond of alcohols.

Acknowledgements

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