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Novel reactivity aspects of *cis*-bis(1-alkenyl)platinum(II) compounds of the type $Pt(CH_2(CH_2)_nCH{=}CH_2)_2L_2$ (where L_2 = dppp, dppe, dppm and n = 1, 2)

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ABSTRACT

We describe the synthesis, structure and reactivity of novel bis(1-alkenyl)platinum(II) complexes, $Pt[CH_2(CH_2)_nCH{=}CH_2]_2L_2$ (where L_2 = dppp, dppe, dppm and n = 1, 2). The stability of the title complexes with the different ligands is discussed. The steric, chelating and electronic properties of the ligands have a significant impact on the structure as well as on the reactivity of the complexes. Novel reactions with elemental sulfur and carbon dioxide are described and discussed.

1. Introduction

Metal–alkenyls are an interesting class of compound in organometallic chemistry, which have been shown to be key intermediates in many catalytic reactions and are also useful precursors with many applications [1]. Recently we have shown that these compounds can undergo ring-closing metathesis reactions (RCM) in the presence of Grubbs' catalysts to produce novel medium to large metallacycloalkanes in high yields [2]. Interestingly, the bis(1-alkenyl)platinum(II) complexes have been shown to undergo selective and quantitative isomerization to their (2-alkenyl)platinum(II) analogs [3]. The formation of stable metal–η^3–allyl complexes from the reactive metal–alkenyl complexes have been also reported [4]. We have previously reported various other reactions such as oxidative addition, insertion of carbon monoxide, transmetalation and thermal decomposition studies of some selected bis(1-alkenyl)platinum(II) complexes [5]. It has also been shown that these title compounds are useful precursors in making heterobimetallic mixed metal carbonyl clusters of the type $PtRu_2$ and Pt_2Ru [6]. The present article describes in detail the synthesis, structure and novel reactivity of the title compounds. The factors that influence the reactivity, as well as structural features are also discussed.

2. Results and discussion

All the metal–alkenyl complexes (**2**–**9**) were prepared either from $[COD]PtCl_2$ or their corresponding haloplatinum(II) precursors (**1a**–**d**) using the well known Grignard route as shown in Scheme 1 [2–4]. It was found that the former route was much superior to the later one. All the products were characterized by analytical and spectroscopic techniques. The structures of **1b** and **9** in the solid state were determined by the single crystal X-ray analysis (Figs. 1 and 2).

The stability of metal–alkenyls strongly depends on various factors such as the nature of donor ligand, solvent, light and temperature. The stability of the complexes with donor atoms increases along the series: diphosphine >> tertiary phosphine > COD > 1,10-phenanthroline > CO. The chelating diphosphines (e.g., dppe, dppp, dppm) imparts an outstanding stability to the metal carbon bonds relative to the other ligands. The monophosphine complexes are relatively stable compared to the corresponding complexes with N donor ligands such as 1,10-phenanthroline and bipyridyl, which are very sensitive to the halogenated solvents, light and heat. Thermolysis of these bis(1-alkenyl)platinum(II) compounds produce different organic products, depending on the experimental conditions [3,5]. It is interesting to note that the length of 1-alkenyl chains did not appear to be a significant factor in the stability of the bis(1-alkenyl)metal complexes.

The reactivity of metal–alkenyls with terminal pendant alkene groups is significantly different from their analogous metallacycloalkanes and metal–alkyl compounds. Thermal

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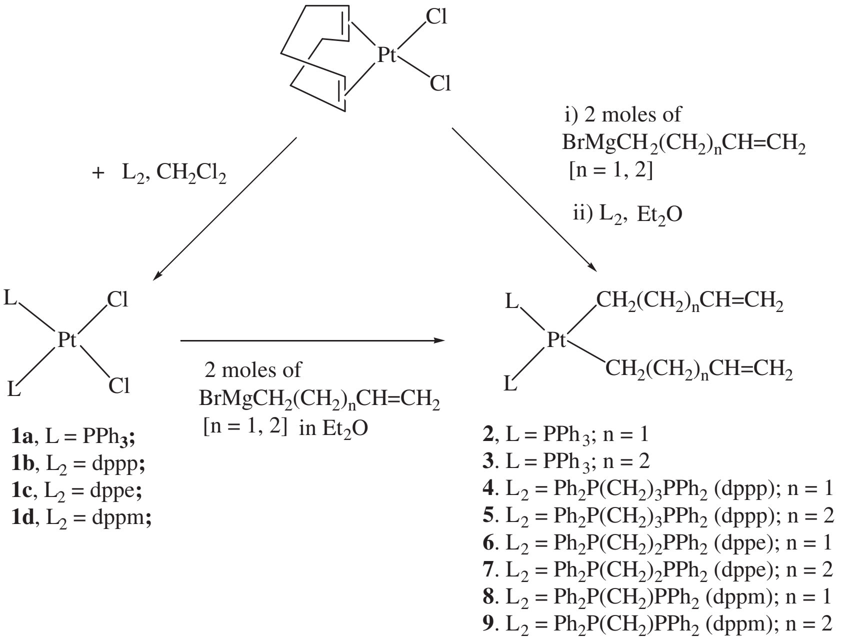


Scheme 1.

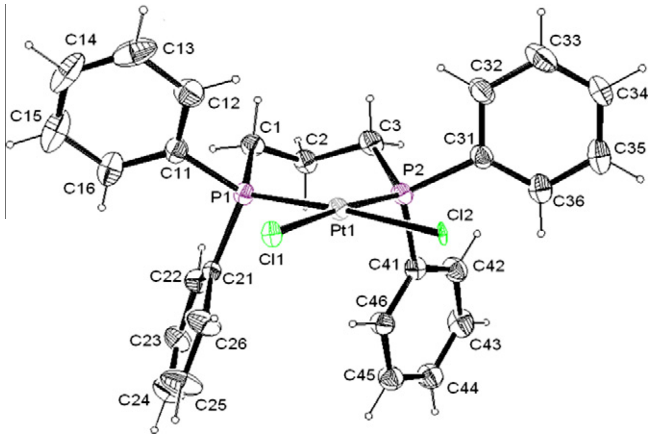


Fig. 1. Molecular structure of **1b** (ORTEP diagram), showing atom-numbering scheme. One benzene solvent molecule is omitted. Ellipsoids are drawn at 30% probability level. Selected bond lengths (Å) and selected bond angles (°): Pt(1)–P(1) 2.247(3); Pt(1)–P(2) 2.241(2); Pt(1)–Cl(1) 2.3927(18); Pt(1)–Cl(2) 2.4207(17); P(2)–Pt(1)–P(1) 94.23(9); P(1)–Pt(1)–Cl(l) 89.87(8); Cl(1)–Pt(1)–Cl(2) 86.87(7).

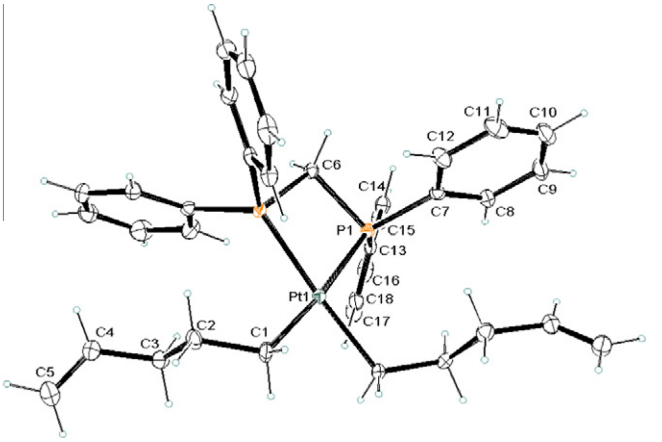


Fig. 2. Molecular structure of **9** (ORTEP diagram), showing atom-numbering scheme. Ellipsoids are drawn at 30% probability level. Selected bond lengths (Å) and selected bond angles (°): Pt(1)–P(1) 2.3025(7); Pt(1)–P(2) 2.3025(7); Pt(1)–C(1) 2.100(3); Pt(1)–C(6) 2.100(3); C(4)=C(5) 1.315(5); C(9)=C(10) 1.377(5); P(2)–Pt(1)–P(1) 73.45(4); C(1)–Pt(1)–C(6) 85.27(17); P(1)–Pt(1)–C(l) 100.66(9).

decomposition of bis(1-alkenyl)platinum(II) complexes has been reported leading to the formation of interesting organic product distribution through β-hydrogen elimination and/or reductive elimination under different experimental conditions [5–7].

2.1. Isomerization of bis(1-alkenyl)platinum(II) complexes to bis(2-alkenyl)platinum(II)

Recently, we have shown that heating the 1-alkenyl complexes *cis*-[Pt(1-alkenyl)$_2$(dppp)] (**5**) [alkenyl = 1-pentenyl and 1-octenyl] to 100 °C gave a quantitative isomerization to the corresponding 2-alkenyl complexes *cis*-[Pt(2-alkenyl)$_2$(dppp)] (**10**) (Eq. (1)). Similar to the isomerization reactions with dppp complexes [3], dppe complexes (**7**) have undergone the quantitative isomerization reaction to give **11** under the similar experimental conditions. And it has been found that this isomerization is strongly dependent on the concentration of the bis(1-alkenyl) complex in solution, the length of alkenyl chains as well as the nature of ligand, L$_2$. When the ligand is dppm, the complex *cis*-[Pt(1-pentenyl)$_2$(dppm)] (**9**) showed the formation of a mixture of unidentified products including the expected *cis*-[Pt(2-pentenyl)$_2$(dppm)]. This could be due to the strain in the four-membered platinacycle with the chelating dppm ligand and thus forming dimeric platinum–alkenyls with bridging dppm. The new 2-alkenyl complexes were fully characterized by analytical and spectroscopic methods. Interestingly, ^{31}P NMR spectra of these complexes indicated the broad signals in the range of δ 46.3–46.8, which suggest a mixture of different isomers (E/E, E/Z, and Z/Z) similar to the formation of **10** [3]. The single crystal X-ray analysis confirmed that **11** is a 2-alkenyl compound and therefore that isomerization has occurred (Fig. 3). It shows that the two alkenyl chains are different where the alkene H atoms are *cis* to each other in one chain, whereas the other shows *trans*-positioned H atoms within the same molecule. Bond lengths and angles of **11** are consistent with compound **10** [3].

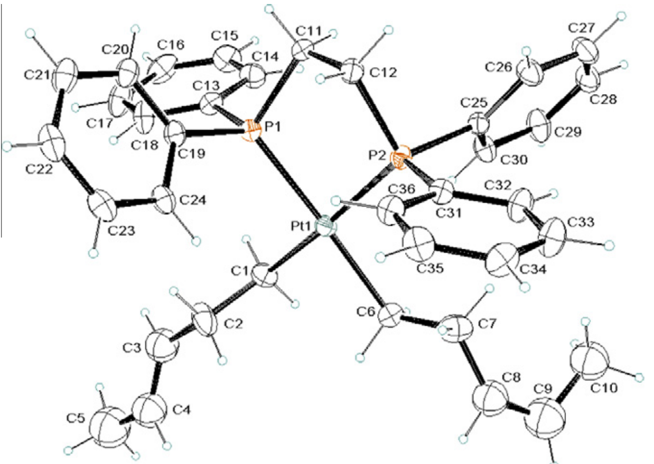
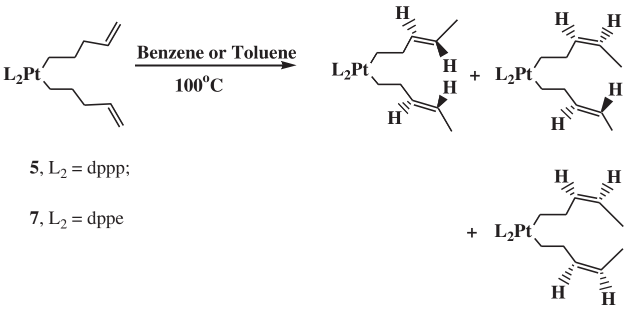


Fig. 3. Molecular structure of **11** (ORTEP diagram), showing atom-numbering scheme. Ellipsoids are drawn at 30% probability level. Selected bond lengths (Å) and selected bond angles (°): Pt(1)–P(1) 2.2667(18); Pt(1)–P(2) 2.2866(18); Pt(1)–C(1) 2.134(8); Pt(1)–C(6) 2.085(8); C(3)═C(4) 1.318(9); C(8)═C(9) 1.267(9); P(2)–Pt(1)–P(1) 84.40(6); C(1)–Pt(1)–C(6) 83.4(4); P(1)–Pt(1)–C(l) 93.0(3).



5, L_2 = dppp;

7, L_2 = dppe

10, L_2 = dppp;

11, L_2 = dppe

(1)

Similar to thermolysis in solution, the UV-irradiation studies of bis(1-pentenyl)platinum(II) complexes clearly revealed the formation of bis(2-pentenyl)platinum(II)(L_2) analogs (**10**, L_2 = dppp and **11**, L_2 = dppe) as major products through an irreversible isomerization. Thermolysis of these isomerization products in the solid state at 175 °C yielded some unexpected organic products including 2-pentene and 2,4-pentadiene as well as some other products in the GC, which were not observed with the precursor compounds.

2.2. Reaction with elemental sulfur

Platinum containing sulfur compounds are known in the literature [8]. Most of the compounds were either ionic or polysulfide compounds. The reaction of elemental sulfur with the title compounds was aimed at the insertion of sulfur into the metal–carbon bonds. However, the reaction gave the platinacyclosulfides as a mixture of products with platinacyclopentasulfide being the major product (Eq. (2)). ^{31}P NMR of the reaction mixture clearly showed the formation of very close singlets for the different platinacycles with different ring sizes, which show similar J_{Pt-P} values. Mass spectral data of the crude reaction mixture clearly indicated the presence of mass fragments with different platinacyclosulfides i.e. L_2PtS_6, L_2PtS_5, L_2PtS_4, L_2PtS_3 and L_2PtS_2 (where L_2 = dppp). It is also well known that the elemental sulfur, S_8 exists as S_4 or S_5 in polar solvents [9]. The organic products were found to be 1-alkenes, 2-alkenes, dienes and traces of unidentified species from the reaction mixtures. The single crystal X-ray analysis confirmed the formation of platinacyclotetrasulfide, PtS_4(dppp) (**12**) as shown in Fig. 4.

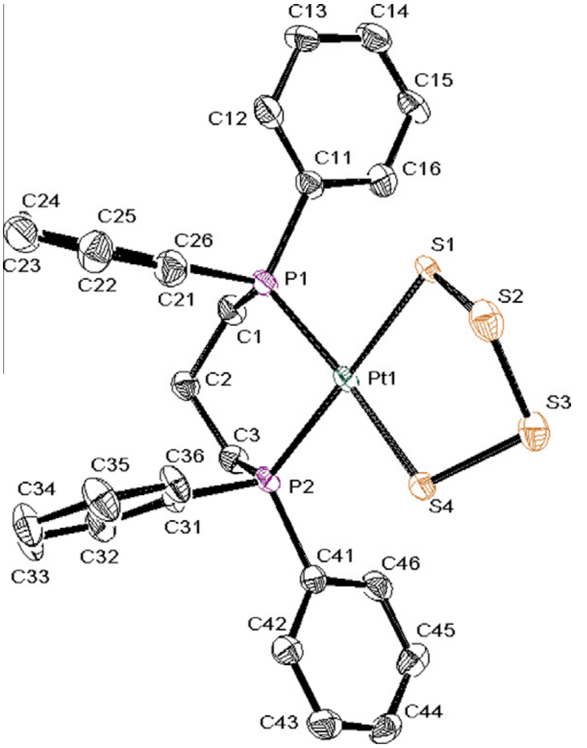
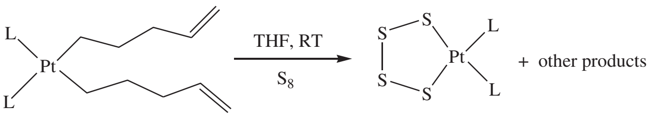


Fig. 4. Molecular structure of **12** (ORTEP diagram), showing atom-numbering scheme. Ellipsoids are drawn at 25% probability level. Selected bond lengths (Å) and selected bond angles (°): Pt(1)–P(1) 2.269(3); Pt(1)–P(2) 2.269(2); Pt(1)–S(1) 2.358(2); Pt(1)–S(4) 2.357(3); P(2)–Pt(1)–P(1) 91.00(9); P(1)–Pt(1)–S(l) 88.61(9); S(1)–Pt(1)–S(4) 93.11(9).



5, L_2 = dppp

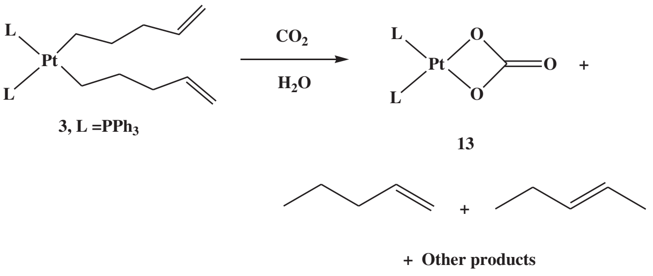
12

(2)

2.3. Reaction with CO_2

Attempts were made to study the insertion reactions with CO_2 using various platinum–alkenyl complexes containing different ligands such as PPh_3, dppe and dppp, but all these reactions were found to be very slow at room temperature. However, the CO_2 inserted products were difficult to isolate as these compounds were found to be very sensitive to the experimental conditions.

In the presence of CO_2 and moisture, the formation of the corresponding known platinum carbonate complexes (**13**) [10] in good yields was evident during the reaction with **3** (Eq. (3)). This could be due to the cleavage of platinum–carbon bonds by the *in situ* formed weak carbonic acid from CO_2–H_2O mixture. The organic products were identified as 1-alkenes (70%), 2-alkenes (12%), the corresponding dienes (2%) and the products with high retention time (16%). The single crystal X-ray analysis indicated the formation of **13** and the bond lengths and bond angles are similar to the literature reports for this compound [10].



Reaction with CO_2

(3)

2.4. Discussion on the crystallographic data of compounds **1b**, **9**, **11**, **12** and **13**

Intensity data for the single crystals of compounds **1b** (CCDC number 674790), **9** (CCDC number 674788), **11** (CCDC number 674787), **12** (CCDC number 674789) and **13** (CCDC number 674786) were collected at 113 K on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The crystallographic data of these compounds are summarized in Table 1.

The bond lengths and bond angles of the solvated crystal structure of **1b** were almost identical with the reported structure [12]. The Pt–P and Pt–C bond lengths in **9** and **11** were found in the range of 2.3025(7)–2.2667(18) and 2.085(8)–2.134(8) respectively (Figs. 2 and 3). But the Pt–P bond lengths of **1b**, **12** and **13** were found to be in the range of 2.247(3)–2.297(18) (Figs. 1, 4 and 5), which are slightly shorter than the bond lengths of **9** and **10**. An analog to the crystal structure of **12** was reported using dppe ligand [13] and it is found that some of the bond lengths and bond angles of these complexes were slightly different to each other. This can be explained by the influence of electronegative atoms attached to the metal. The C=C bond lengths in **9** and **11** showed 1.315(5), 1377(5) and 1.267(9), 1.318(9) respectively. In **13**, the bond length in C=O was 1.208(8), which is significantly shorter that the other C–O bond lengths [1.323(9) and 1.369(9)].

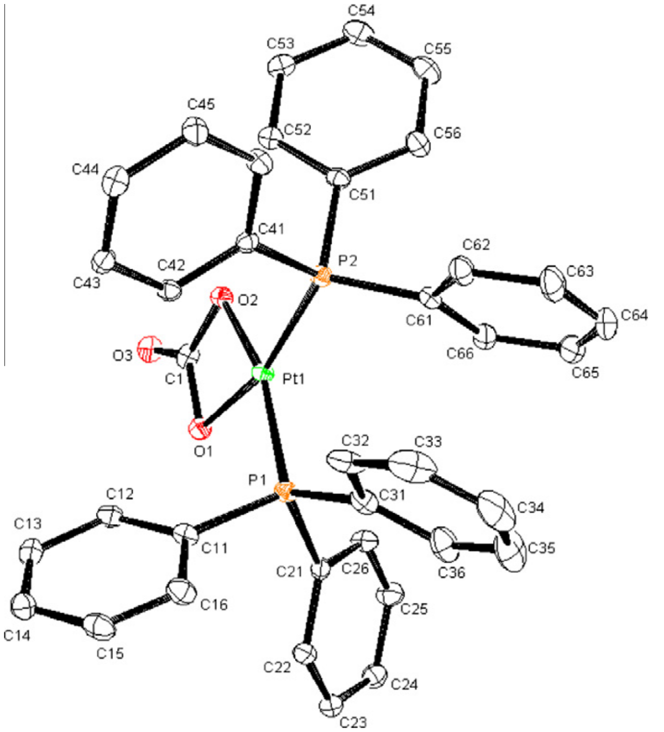


Fig. 5. Molecular structure of **13** (ORTEP diagram), showing atom-numbering scheme. Ellipsoids are drawn at 25% probability level. Selected bond lengths (Å) and selected bond angles (°): Pt(1)–P(1) 2.2297(18); Pt(1)–P(2) 2.2524(18); Pt(1)–O(1) 2.042(4); Pt(1)–O(2) 2.063(5); P(2)–Pt(1)–P(1) 99.66(7); P(1)–Pt(1)–O(I) 98.78(14); O(1)–Pt(1)–O(4) 65.28(19).

Table 1
X-ray data and refinement parameters for compounds **1b**, **9**, **11**, **12** and **13**.

Compound	**1b**	**9**	**11**	**12**	**13**
Structure formula	$C_{27}H_{26}Cl_2P_2Pt{\cdot}0.5C_6H_6$	$C_{35}H_{40}P_2Pt$	$C_{36}H_{42}P_2Pt$	$C_{27}H_{26}P_2PtS_4{\cdot}2CHCl_3$	$C_{36}H_{30}O_3P_2Pt{\cdot}C_2H_2Cl_2$
Formula weight	717.46	717.70	731.73	974.48	864.57
Data collection temperature (K)	173(2)	133(2)	113(2)	133(2)	113(2)
Crystal system, space group	monoclinic, $P2_1/n$	monoclinic, $C2/c$	monoclinic, $P2_1/c$	monoclinic, $P2_1/c$	triclinic, $P\bar{1}$
a (Å)	11.7212(2)	17.3672(2)	12.2411(2)	12.9880(4)	10.5215(2)
b (Å)	15.0029(5)	8.2433(1)	14.6320(2)	14.0947(5)	12.1655(3)
c (Å)	16.1048(6)	22.4767(3)	17.9071(3)	19.7921(6)	15.2639(4)
α (°)	90	90	90	90	85.629(1)
β (°)	98.541(2)	105.326(1)	95.694(1)	98.558(1)	71.541(1)
γ (°)	90	90	90	90	70.453(1)
V (Å^3)	2800.7(2)	3103.40(7)	3191.55(9)	3582.8(2)	1745.48(7)
Z	4	4	4	4	2
D_{calc}, calculated density (g cm^{-3})	1.702	1.536	1.523	1.807	1.645
Absorption coefficient μ (mm^{-1})	5.333	4.646	4.519	4.708	4.300
F(0 0 0)	1404	1432	1464	1904	852
Crystal size (mm)	0.06 × 0.08 × 0.14	0.02 × 0.03 × 0.06	0.07 × 0.09 × 0.12	0.02 × 0.03 × 0.05	0.07 × 0.08 × 0.11
θ Range for data collection	4.03–26.02	3.45–25.34	3.39–25.67	2.89–25.07	3.13–25.66
Limiting indices	−14, 12; ±18; ±19	±20; ±9; ±27	±14; ±17; ±21	±15; ±16; ±23	±12; ±14; ±18
Reflections collected /unique	48 280/5483	41 691/2829	82 791/6031	40 532/6320	32 837/6543
No. of parameters/restraints	317/0	174/0	325/4	352/0	402/0
Extinction coefficient	0.0004(3)	0.0003(5)	0.0005(2)	0.0002(1)	0.0026(5)
Goodness-of-fit (GOF) on F^2	1.052	1.079	1.037	1.026	1.028
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0512 wR_2 = 0.1292	R_1 = 0.0207 wR_2 = 0.0409	R_1 = 0.0426 wR_2 = 0.1090	R_1 = 0.0580 wR_2 = 0.1252	R_1 = 0.0463 wR_2 = 0.0983
R indices (all data)	R_1 = 0.0821 wR_2 = 0.1475	R_1 = 0.0207 wR_2 = 0.0424	R_1 = 0.0602 wR_2 = 0.1199	R_1 = 0.0959 wR_2 = 0.1408	R_1 = 0.0752 wR_2 = 0.1089
Largest difference peak and hole (e Å^{-3})	2.943/−1.448	2.107/−0.661	1.979/−1.453	1.957/−1.617	1.939/−1.883

The P–Pt–P bond angles of compounds **9** [73.45(4)] and **11** [84.40(6)] were found to be shorter than the other compounds, **1b** [94.23(9)], **12** [91.00(9)] and **13** [99.66(7)]. In **10**, the olefinic protons were found to be *cis* to each other in one chain and *trans* to each other in another chain.

In conclusion, a variety of bis(alkenyl)platinum(II) complexes with different donor ligands have been made and it is found that the stability of these complexes depends on the nature of ligand. The novel reactivity aspects of these complexes reveal that they are promising precursors in many interesting reactions.

3. Experimental

3.1. General

All manipulations were carried out under a nitrogen atmosphere unless otherwise stated. The solvents were commercially available and distilled from dark purple solutions of sodium/benzophenone ketyl. ^{1}H and ^{31}P NMR spectra were recorded on a Bruker DMX-400 spectrometer and all ^{1}H chemical shifts are reported relative to the residual proton resonance in the deuterated solvents (all at 298 K, C_6D_6). Microanalyses were conducted with a Thermo Flash 1112 Series CHNS–O Analyzer instrument. GC analyses were carried out using a Varian 3900 gas chromatograph equipped with an FID and a 30 m × 0.32 mm CP-Wax 52 CB column (0.25 μm film thickness). The carrier gas was helium at 5.0 psi. The oven was programmed to hold at 32 °C for 4 min and then to ramp to 200 °C at 10 °/min and hold 5 min. GC–MS analyses for peak identification were performed using an Agilent 5973 gas chromatograph equipped with MSD and a 60 m × 0.25 mm Rtx-1 column (0.5 μm film thickness). The carrier gas was helium at 0.9 ml/min. The oven was programmed to hold at 50 °C for 2 min and then ramp to 250 °C at 10 °/min and hold 8 min. Pt(COD)Cl_2 [11], L_2PtCl_2 [14] (L = PPh_3 and L_2 = dppp, dppe and dppm) (**1a–d**), 1-alkenyl Grignard reagents ($BrMgCH_2(CH_2)_nCH{=}CH_2$; n = 1, 2) were prepared according to literature procedures [15]. The compounds *cis*-[Pt(1-butenyl)$_2$(PPh_3)$_2$] (**2**) [2c], *cis*-[Pt(1-pentenyl)$_2$(PPh_3)$_2$] (**3**) [2c], *cis*-[Pt(1-pentenyl)$_2$(L_2)] {**5**, L_2 = dppp [2a,2b]; **7**, L_2 = dppe [5]}, *cis*-[Pt(2-pentenyl)$_2$(dppp)] (**10**) [3] and *cis*-(carbonato-κ^2O,O′)bis(triphenylphosphine-κP)platinum(II) (**13**) were prepared as mentioned earlier.

3.2. Synthesis of compounds **4**, **6**, **8**, **9**, **11–13**

3.2.1. cis-[Pt(1-butenyl)$_2$(dppp)] (**4**)

In a Schlenk flask, Pt(COD)Cl_2 (316 mg, 0.818 mmol) in diethyl ether (20 mL) was cooled to T = −78 °C and 1-butenyl Grignard reagent (2.9 mL of 0.85 M, 2.454 mmol) was added. The solution was brought to ca. 0 °C and then stirred until the solution became clear. To this, dppp (337 mg, 0.818 mmol) was added and the reaction mixture stirred for 36 h until a clear solution is formed. The excess Grignard reagent was removed by hydrolyzing the reaction mixture with 5 ml of saturated aqueous NH_4Cl at −78 °C. The aqueous layer was washed with 3 × 5 ml of dichloromethane before the organic layer was separated. All the volatiles in the flask were removed under reduced pressure and the residue obtained was recrystallized from a CH_2Cl_2/hexane mixture (1:2) at −10 °C for 48 h. The colorless crystalline solid was separated by decanting the mother liquor and dried under vacuum. For **4**; m.p. 132–134 °C; yield 97%, *Anal.* Calc. for $C_{35}H_{40}P_2Pt$: C, 58.57; H, 5.62. Found: C, 58.66; H, 5.72%. ^{1}H NMR δ 7.26–7.76 (m, 20H, Ph); 5.42–5.63 (m, 2H, =2CH); 4.40–4.53 (m, 4H, $=CH_2$); 2.41–2.59 (m, 6H, P–CH_2); 0.62–1.93 (m, 8H, –CH_2); ^{31}P{^{1}H} NMR: 3.44 (s) (J_{Pt-P} = 1623 Hz).

3.2.2. cis-[Pt(1-butenyl)$_2$(dppe)] (**6**)

A similar procedure was followed as described above using Pt(COD)Cl_2 (356 mg, 0.951 mmol) in diethyl ether (20 mL), 1-butenyl Grignard reagent (3.4 mL of 0.85 M, 2.853 mmol) and dppe (379 mg, 0.951 mmol). Yield: 95%. m.p. 143–145 °C, *Anal.* Calc. for $C_{36}H_{42}P_2Pt$: C, 59.09; H, 5.79. Found: C, 58.82; H, 5.74%. ^{1}H NMR: δ 7.36–7.91 (m, 20H, Ph), 5.55–5.71 (m, 2H, =CH), 4.69–4.80 (m, 4H, $=CH_2$), 1.99–2.17 (m, 4H, P–CH_2), 1.25–1.85 (m, 12H, CH_2); ^{31}P NMR: δ 45.9 (s) (J_{Pt-P} = 1641 Hz).

3.2.3. cis-[Pt(1-butenyl)$_2$(dppm)] (**8**)

A similar procedure was followed as described above using Pt(COD)Cl_2 (386 mg, 1.031 mmol) in diethyl ether (20 mL), 1-butenyl Grignard reagent (3.65 mL of 0.85 M, 3.093 mmol) and dppm (396 mg, 1.031 mmol). The yield of the white crystalline solid was 92%, m.p. 154–56 °C (dec), *Anal.* Calc. for $C_{33}H_{36}P_2Pt$: C, 57.47; H, 5.26. Found: C, 57.64; H, 5.28%. ^{1}H NMR: δ 7.26–7.96 (m, 20H, Ph), 5.60–5.76 (m, 2H, =CH), 4.71–4.82 (m, 4H, $=CH_2$), 4.12–4.29 (m, 2H, P–CH_2), 1.52–2.07 (m, 8H, CH_2); ^{31}P NMR: δ −32.8 (s) (1296 Hz).

3.2.4. cis-[Pt(1-pentenyl)$_2$(dppm)] (**9**)

Compound **9** was prepared in the same fashion as compound **4** utilizing Pt(COD)Cl_2 (426 mg, 1.138 mmol) in diethyl ether (20 mL), 1-pentenyl Grignard reagent (2.75 mL of 1.25 M, 3.414 mmol) and dppm (434 mg, 1.138 mmol). The yield was 94% of the white crystalline solid, m.p. 118–120 °C (dec), *Anal.* Calc. for $C_{35}H_{41}P_2Pt$: C, 58.57; H, 5.62. Found: C, 58.82; H, 5.72%. ^{1}H NMR: δ 7.29–7.90 (m, 20H, Ph), 5.62–5.78 (m, 2H, =CH), 4.73–4.85 (m, 4H, $=CH_2$), 4.07–4.25 (m, 2H, P–CH_2), 1.52–2.07 (m, 12H, CH_2); ^{31}P NMR: δ −32.9 (s) (1296 Hz).

3.2.5. cis-[Pt(2-pentenyl)$_2$(dppe)] (**11**)

A Schlenk flask was charged with 154 mg (0.211 mmol) of **7** in 10 mL of toluene and the mixture was heated at 110 °C for 125 h under reduced pressure. The reaction was monitored by ^{1}H NMR. All the volatiles were removed from the pale yellow brown reaction mixture. The product was recrystallized from a CH_2Cl_2/hexane mixture (3:5 mL) at −10 °C for 48 h. to give pure **11** as crystalline colorless solid. Yield: 128 mg (83%). m.p. 153–155 °C, *Anal.* Calc. for $C_{36}H_{42}P_2Pt$: C, 59.09; H, 5.79. Found: C, 59.32; H, 5.84%. ^{1}H NMR: δ 6.76–7.74 (m, 20H, Ph), 5.21–5.58 (m, 4H, =CH), 1.83–2.03 (m, 4H, P–CH_2), 0.68–1.77 (m, 14H, CH_2 and CH_3); ^{31}P NMR: δ 46.3–46.8 (m) (J_{Pt-P} = 1642 Hz).

3.2.6. Platinacyclotetrasulfide (**12**)

A solution of *cis*-[Pt(1-pentenyl)$_2$(dppp)] (245 mg, 0.328 mmol) and elemental sulfur (168 mg, 0.654 mmol) in THF (10 mL) was stirred at room temperature for 3 days. The solvent was removed in vacuo, and the product was isolated from a preparative TLC plate using CH_2Cl_2 as an eluent and recrystallized from *n*-hexane/CH_2Cl_2 (5:1) at T = −30 °C. The pure yellow brown crystalline solid was isolated as major product and dried under vacuo for 3 h. Yield: 176 mg (72%). m.p. 174–176 °C (dec), *Anal.* Calc. for $C_{27}H_{26}P_2S_4Pt$: C, 44.07; H, 3.56. Found: C, 44.16; H, 3.62%. ^{1}H NMR: δ 7.31–7.86 (m, 20H, Ph), 1.92–2.77 (m, 6H, P–CH_2); ^{31}P NMR: δ −5.4 (s) (2706 Hz).

3.2.7. General procedure for UV-irradiation studies

UV-irradiations were carried out with an Englehard Hanovia Lamp (125 W) at a distance of 16 cm from the reaction tube under the constant water circulation. The John–Young NMR tubes containing sample solutions of **10** (102 mg, 0.136 mmol) and **11** (96 mg, 0.131 mmol) in toluene-d^8 were irradiated for 8 h. These reactions were monitored by ^{1}H and ^{31}P NMR until the signals for the starting materials (i.e. 1-alkene protons) disappeared.

3.2.8. General procedure for CO_2 insertion reactions

Compound **3** (196 mg, 0.228 mmol) was dissolved in a wet toluene solution (20 mL). After bubbling CO_2 through the contents of the flask for 5–6 min, the solution was stirred at 50 °C under ambient pressure of carbon monoxide (balloon). After 72 h, the solvent was removed under the reduced pressure and washed with 10 mL of Et_2O. The obtained residue was filtered and recrystallized from a CH_2Cl_2/hexane mixture (2:1 v/v) to give compound **13**. Yield 71% (126 mg). The spectroscopic and analytical characterization data were found to be similar to the earlier reports [10].

4. Supplementary material

CCDC 674790, 674788, 674787, 674789, and 674786 contain the supplementary crystallographic data for **1b**, **9**, **11**, **12**, and **13**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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