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Studies on reactivity of platinum-based heterobimetallic carbonyl clusters

SADHANA VENKATESH, CHINDULURI SRAVANI, R.R. STEBY,
KARI VIJAYAKRISHNA and AKELLA SIVARAMAKRISHNA*

Department of Chemistry, School of Advanced Sciences, VIT University, Vellore, India

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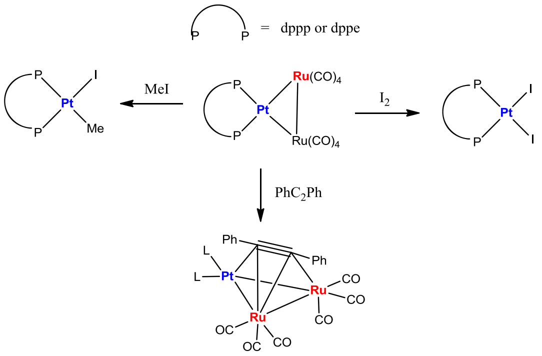

Reactivity of platinum-based trinuclear carbonyl clusters of the type $L_2PtRu_2(CO)_8$, where L_2 = 1,3-bis(diphenylphosphino)propane (dppp) and 1,2-bis(diphenylphosphino)ethane (dppe), is described. Oxidative addition reactions of these bimetallic carbonyl clusters with methyl iodide reveal the formation of products such as L_2PtMeI and L_2PtI_2 and $Ru_3(CO)_{12}$. On heating with diphenylacetylene, $L_2PtRu_2(CO)_8$ gave high yields of the corresponding products $L_2PtRu_2(CO)_6(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)$ ($L = PPh_3$ or L_2 = dppe or dppp). Hydrogenation of $(dppe)PtRu_2(CO)_6(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)$ yields stilbene and a new carbonyl cluster, $[(dppe)_2Pt_2Ru(CO)_4]$ possessing two platinum centers of the type $\{Pt_2Ru\}$. All the products were isolated and characterized by FT-IR, NMR, and mass spectral analysis.

The present article describes the synthesis and reactivity of platinum-based trinuclear carbonyl clusters $L_2PtRu_2(CO)_8$ where L_2 = 1,3-bis(diphenylphosphino)propane (dppp) and 1,2-bis(diphenylphosphino)ethane (dppe). Oxidative addition reactions of these bimetallic carbonyl clusters with methyl iodide yield products such as L_2PtMeI and L_2PtI_2 and $Ru_3(CO)_{12}$. On heating with diphenylacetylene, $L_2PtRu_2(CO)_8$ gives high yields of the corresponding products like $L_2PtRu_2(CO)_6(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)$ ($L = PPh_3$ or L_2 = dppe or dppp). Hydrogenation of $(dppe)PtRu_2(CO)_6(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)$ yields stilbene and a new carbonyl cluster, $[(dppe)_2Pt_2Ru(CO)_4]$ possessing two platinum centers of the type $\{Pt_2Ru\}$. All the products were isolated and characterized by FT-IR, NMR, and mass spectral analysis.

Keywords: Heterobimetallic carbonyl clusters; Reactivity; Oxidative addition; Mass spectral analysis

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*Corresponding author. Email: asrkrishna@vit.ac.in

1. Introduction

Platinum-based mixed metal clusters exhibit interesting structural features and catalytic applications [1–3]. Also, they have potential to act as models for mixed metal catalysts [4]. A good number of multi-metallic clusters including $\{Ru_3Pt\}$, $\{Ru_3Pt_2\}$, $\{Ru_2Pt\}$, and $\{RuPt_2\}$ [5, 6] cores are known and their rich chemistry has been discussed by earlier workers [7]. These clusters undergo rearrangement reactions and dynamic fluxionality within clusters. Most of the transformations were based on either cluster expansion by aggregation or degradation through splitting larger clusters into smaller ones [8]. Addition and/or substitution reactions of various ligands were also reported with phosphines, diphosphines, thioethers, carbonyls, 1,5-cyclooctadiene (COD), alkynyls, vinylidenes, etc. [3]. Supported Pt/Ru/alumina catalysts have significant applications in petroleum refining and platinum–ruthenium electrodes are used to catalyze methanol oxidation in fuel cells [9]. Platinum–ruthenium clusters are catalysts for hydrogenation and hydrosilylation of alkynes [10]. The self-assembly of $[Pt_{3n}(CO)_{6n}]^{2-}$ ($n = 4$–8) clusters with different dimensional materials has resemblance to molecular metal wires morphologically and functionally [11]. Some of the Ru-based carbonyl clusters were utilized as methanol tolerant electrocatalysts for oxygen reduction [12]. Bimetallic MgO-supported $Pt_3Ru_6(CO)_{21}(\mu_3\text{-}H)(\mu\text{-}H)_3$ clusters were used as hydrogenation catalysts [13].

We recently illustrated a facile route for the high-yield synthesis of mixed trinuclear metal carbonyl clusters $[PtRu_2(CO)_8L_2]$ ($L = PPh_3$; L_2 = dppe or dppp) using the reaction of $[Ru_3(CO)_{12}]$ with $[PtL_2(1\text{-alkenyl})_2]$ [14] (scheme 1). This article describes the reactivity of Pt-based heterobimetallic carbonyl clusters **5** and **6**.

2. Results and discussion

2.1. *Synthesis and characterization*

Several research groups have extensively investigated the synthesis and reactivity patterns of platinum-based clusters [5–7, 15]. We recently reported a facile and high-yield synthesis of platinum-based trinuclear heterobimetallic carbonyl clusters [14] using bis(1-alkenyl)Pt (II) complexes as precursors [16, 17]. This article describes oxidative addition with methyl halide, iodination, hydrogenation, and acetylene adducts of the clusters of the type $[L_2PtRu_2(CO)_8]$ (where L_2 = dppp or dppe).

Initially, bis(1-alkenyl)platinum(II) complexes (**3**,**4**) were prepared by reaction of **1** and **2** with appropriate Grignard reagents as shown in scheme 1. The trinuclear carbonyl clusters with a $\{PtRu_2\}$ core $[L_2PtRu_2(CO)_8]$ (where L_2 = dppp (**5**) or dppe (**6**)) were obtained as products upon the reactions of **3–4** with $Ru_3(CO)_{12}$ [14] (scheme 2).

2.2. *Oxidative addition of MeI*

A variety of reactions have been reported with Pt–Ru heterobimetallic clusters [3]. Usually, these clusters undergo oxidation and form L_2PtI_2 immediately after adding iodine in solution.

The major product isolated was found to be PtMeI(dppp) (**7**) showing the corresponding signals in ^{31}P-NMR spectra as two doublets at δ –3.23, –3.37 and 2.03, 2.19 ($J_{\text{Pt-p}} = 3920$

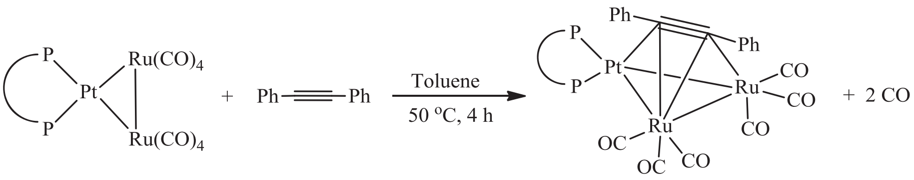
and 1667 Hz, respectively). A similar product was formed even after heating the reaction mixture for several hours at room temperature. The driving force for this reaction could be initial formation of six coordinate platinum(IV) species by oxidative addition of methyl iodide and subsequent reductive elimination to produce **7**. Attempts to isolate and identify the other products generated from this reaction failed. The ^{31}P-NMR spectrum of the crude reaction mixture showed the presence of only **7**, which has a diphosphine unit. Though it is also possible to add methyl iodide at ruthenium centers, the absence of phosphine ligand in the obtained products makes the characterization difficult and no other products could be isolated by column chromatography.

2.3. *Iodination*

Reactions of **5** with iodine yielded **9**, [PtL_2I_2] (where L_2 = dppp), which was characterized by NMR spectroscopy. The ^{31}P-NMR spectra indicated a chemical shift at δ –10.0 ($J_{Pt\text{-}p}$ = 3660 Hz) for [$Pt(dppp)I_2$], which is in agreement with an authentic sample of [$Pt(dppp)I_2$]. The other major product isolated from the reaction was [$Ru_3(CO)_{12}$]. We propose that the reaction proceeds via oxidative addition of halogens to the platinum center by breaking the Pt–Ru bonds. The only isolated product from this reaction was $Pt(dppp)I_2$, which shows a signal in ^{31}P-NMR spectrum at –10.0 ppm (s, $J_{Pt\text{-}p}$ = 3660 Hz) flanked by platinum satellites.

2.4. *Reaction with substituted acetylenes*

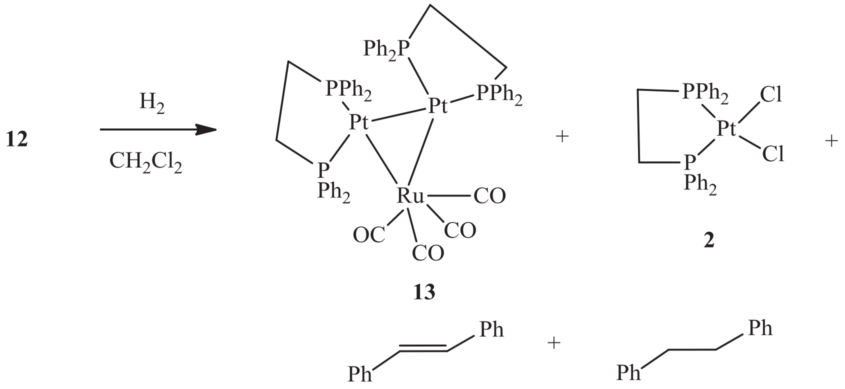
Alkynes are very effective bridging ligands in metal carbonyl cluster complexes and thus their complexes are often the subject of studies on catalytic alkyne hydrogenation [18, 19]. The alkyne complex [$PtRu_5(CO)_{13}(PBu^t_3)(\mu_5\text{-}C)(\mu_3\text{-}PhC_2H)$] can act as a catalyst precursor for the hydrogenation of PhC_2H (phenylacetylene) to styrene and ethylbenzene [20]. The PhC_2Ph complexes [$PtRu_2(CO)_6(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)(dppp)$] (**11**) and [$PtRu_2(CO)_6(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)(dppe)$] (**12**) were prepared and isolated in moderate yields from the reactions of **5** and **6** with PhC_2Ph in toluene solution at 50 °C (equation 1). The clusters **11** and **12** were characterized by IR, NMR spectral, and elemental analysis. ^{31}P-NMR spectra of **11** and **12** exhibited two signals with $J_{Pt\text{-}p}$ = 4725 and 4730 Hz, respectively.



5, L_2 = dppp
6, L_2 = dppe

11, L_2 = dppp
12, L_2 = dppe

2.5. *Hydrogenation of 12*



The product is not stable in chlorinated solvents and produces (dppe)PtCl$_2$ immediately as one of the products. The ^{31}P-NMR spectrum of **13** showed a singlet flanked by two platinum satellites at δ 46.2 ($J_{\text{Pt-p}}$ = 4730 Hz), confirming symmetric nature of two dppe ligands in the molecule. The infrared spectrum did not exhibit any bridging carbonyl group, but confirms the presence of terminal CO ligands with strong absorptions between 2050 and 1966 cm^{-1}. **2** was obtained from the reaction mixture and confirmed by NMR and mass analysis. The reason for the formation of **2** could be due to the reaction of dichloromethane with unstable intermediate cluster species. No diphenylacetylene was observed in the reaction mixture after the hydrogenation reaction. Instead, two products *i.e.* stilbene and 1,2-diphenylethane were also formed during the hydrogenation of **12**. These clusters also may act as catalysts for the hydrogenation of organic substrates.

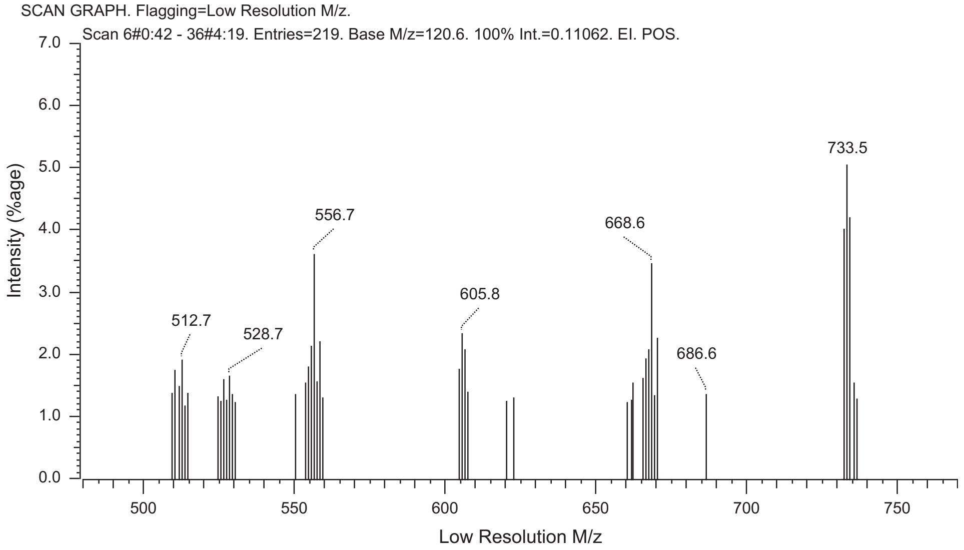


Figure 1. Mass spectrum of **7**.

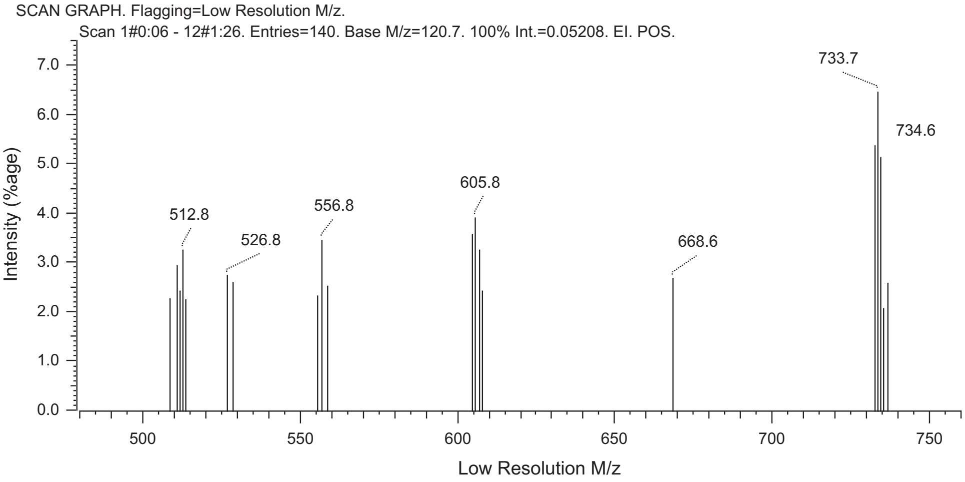


Figure 2. Mass spectrum of **9**.

2.6. *Mass spectral analysis*

Ion formation in FAB arises from charge exchange between the fast-moving incident particles and the neutral molecules in solution to generate $M^{+/-}$ or M^+ and ions [21]. Complexes with halide ligands often lose HX, concomitant with oxidative addition of a carbon–hydrogen bond of a ligand to the metal center, or alternatively, formation of an $[M\text{-}X]^+$ ion is a common ionization route.

Neutral molecules acquire charge via protonation or formation of a cation. In square-planar platinum(II) complexes [Pt(dppp)MeI] in the combination of 3-nitrobenzyl alcohol (3-nba), the primary ionization route is via loss of iodide to give a series of peaks due to

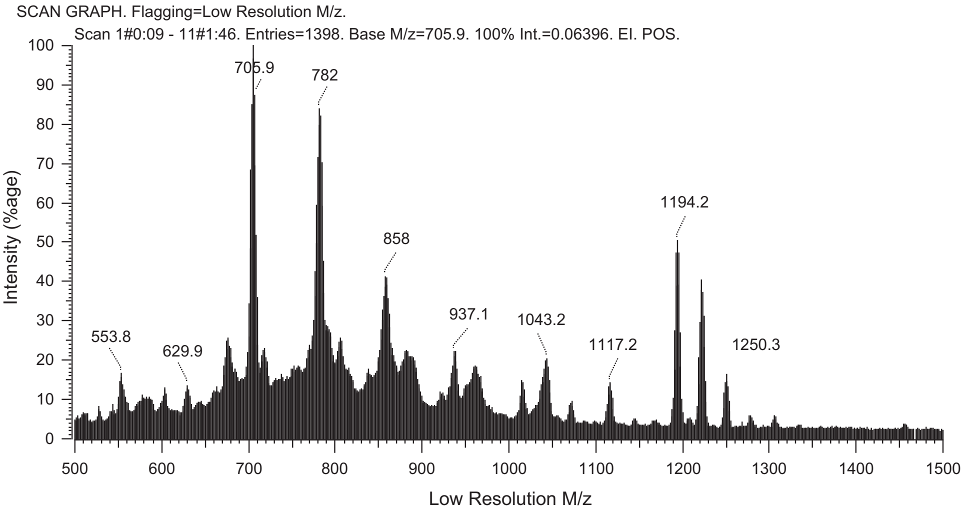


Figure 3. Mass spectrum of **11**.

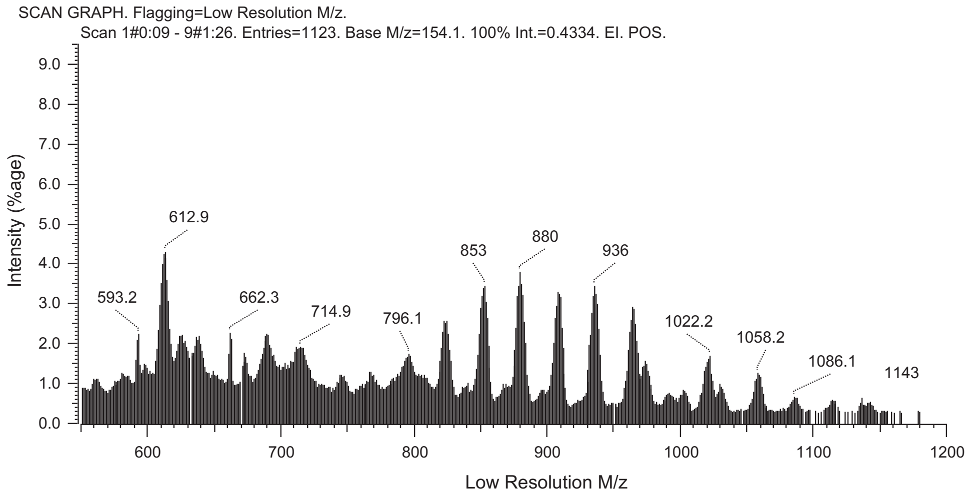


Figure 4. Mass spectrum of **12**.

$[M\text{-}I]^+$ ions and fragments thereof as shown in figure 1. The methyl group is easily eliminated as CH_4 and the hydrogen coming from the phenyl ring of a phosphine and resulting in a cyclometalated complex. Loss of neutral PPh_3 is also a major fragmentation pathway. This is in accord with earlier reports [22].

Figure 1 shows the mass spectrum of the isolated product and its simultaneous dissociated mass fragments of (dppp)PtI ($m/z = 733.5$), (dppp)PtCH_3 ($m/z = 623$), and Pt(dppp)+ ($m/z = 607.4$). No molecular ion peak was observed for **7**. The mass spectrum of **9** shows the formation of fragmented species (dppp)PtI of $m/z = 733.5$ and $(dppp)Pt^+$ ($m/z = 607.4$) as shown in figure 2.

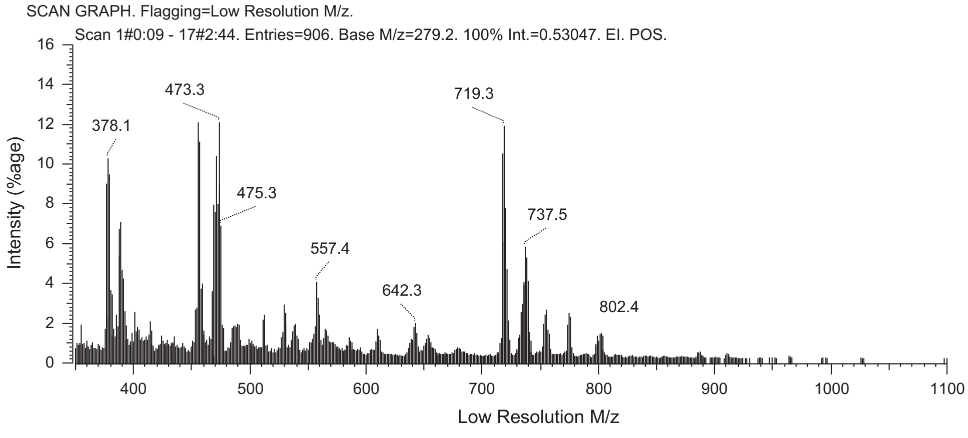
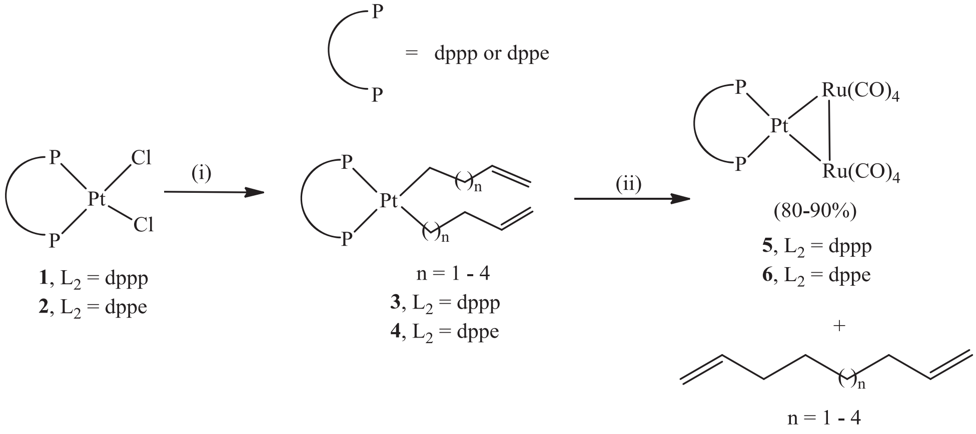
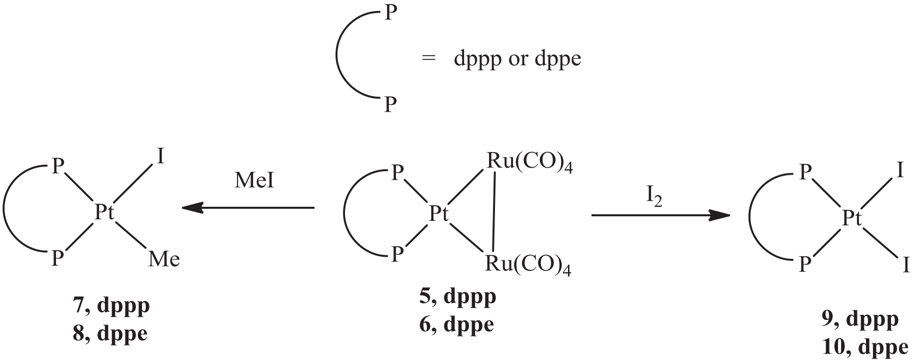


Figure 5. Mass spectrum of **13**.



Scheme 1. (i) RMgCl, R = 1-butenyl, Et_2O, –78 °C; (ii) $Ru_3(CO)_{12}$, Toluene, 80 °C, 8 h.



Scheme 2. Oxidative addition reactions of 5 and 6.

Figures 3 and 4 describe the sequential dissociation of CO from the molecular ion (*m/z* = 1155.94 and 1143.01, respectively, for **11** and **12**) to the corresponding mass fragments of lower mass.

The structure of unexpected product **13** was further confirmed by FAB mass analysis as shown in figure 5. Though the molecular ion was not present, the corresponding fragments such as $[M\text{-dppe}]^+$ at 1029.74, $[(dppe)PtRu(CO)_4]^+$ at 806.61, $[(dppe)PtRu(CO)_3]^+$ at 777.99, $[(dppe)PtRu(CO)_2]^+$ at 750.59, $[(dppe)PtRu(CO)_2]^+$ at 722.58, and $[(dppe)Pt]^+$ at 593.10.

3. Experimental

3.1. *Materials and instruments*

All reactions and manipulations were carried out under an inert atmosphere of dry nitrogen using standard Schlenk and vacuum-line techniques. $[Pt(COD)Cl_2]$ [23] (COD = 1,5-cyclooctadiene), $[Pt(dppp)Cl_2]$ (dpp*p* = 1,3-bis(diphenylphosphino)propane) (**1**), $[Pt(dppe)Cl_2]$

(dppe = 1,2-bis(diphenylphosphino)ethane) (**2**), $[Pt(dppp)\{(CH_2)_3CH=CH_2\}_2]$ (**3**) [16], and $[Pt(dppe)\{(CH_2)_3CH=CH_2\}_2]$ (**4**) [17] were prepared as previously described. $[Ru_3(CO)_{12}]$ and diphenylacetylene (Sigma-Aldrich) were purchased and used as received. $[PtRu_2(CO)_8(dppp)]$ (**5**) and $[PtRu_2(CO)_8(dppe)]$ (**6**) were prepared as reported earlier [14]. The solvents were purchased from commercially available sources and distilled from dark purple solutions of sodium/benzophenone ketyl prior to use.

3.1.1. Nuclear magnetic resonance spectroscopy. ^1H and ^{31}P NMR spectra were recorded on a Bruker DXM-400 spectrometer. All ^1H chemical shifts are reported to the residual proton resonance in the deuterated solvent used. All ^{31}P chemical shifts are ^1H decoupled and referenced to an 85% phosphoric acid external reference at 0 ppm. NMR spectra were recorded on a Bruker Avance DMX-400 spectrometer and operating frequencies were 400.13 MHz (^1H) and 100.61 MHz (^{13}C). All spectra were recorded in $CDCl_3$ solvent. Melting points were measured in sealed capillaries using a Deep vision digital melting point instrument and are uncorrected.

3.1.2. Elemental analysis. Micro analyses were conducted with a Thermo Flash 1112 Series CHNS-O Analyzer instrument.

3.1.3. GC-MS analysis. 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 ramped to 200 °C at 10 °C min^{-1} and held 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^{-1}. The oven was programmed to hold at 50 °C for 2 min and then ramped to 250 °C at 10 °C min^{-1} and held 8 min.

3.1.4. Infrared spectroscopy. Infrared spectra were recorded on a Perkin-Elmer FT-IR spectrometer.

3.1.5. Mass spectrometry. Mass spectral data were obtained using VG70SE with 8 kV acceleration and the FAB gun is an Iontech Saddlefield, using xenon gas and operating at 8 kV. All matrices were made with 3-nitrobenzyl alcohol (nba).

3.2. *Experimental procedures*

3.2.1. Procedure for the preparation of 7, (dppp)PtMeI. A solution of $[PtRu_2(CO)_8(dppp)]$ (302 mg, 0.292 mM) and methyl iodide (42 mg, 0.2958 mM) in dichloromethane (10 mL) was stirred at room temperature for 6 h. The color change was to yellow from orange–red. The solvent was removed in vacuo and the remaining solid was recrystallized from hexane/CH_2Cl_2 (5:1) at $T = 0$ °C to obtain a pale yellow crystalline solid. Yield: 158 mg (88%). m.p. 258–260 °C, Anal. Calcd for $C_{28}H_{29}P_2PtI$: C, 44.87; H, 3.90. Found: C, 44.92; H, 3.94. ^1H NMR: δ 6.99–7.93 (m, 20H, Ph), 1.19 (s, 3H, Pt-CH_3,

$J_{Pt\text{-}H}$ = 13.9 Hz), 1.35–2.11 (m, 6H, CH_2 and P-CH_2), ^{13}C NMR: δ –5.6 (Pt-CH_3), 21.6 (P-CH_2*CH_2*), 33.1 (P-*CH_2*CH_2), 122.0–136.1 (Ph), ^{31}P NMR: δ –3.23, –3.37 and 2.03, 2.19 (two doublets, $J_{Pt\text{-}p}$ = 1667 and 3920 Hz). MS (FAB, *m/z*) = [(dppp)PtI]$^+$ (*m/z* = 733.5), [(dppp)PtCH_3]$^+$ (*m/z* = 623), and [Pt(dppp)]$^+$ (*m/z* = 607.4). The spectroscopic data of **7** were similar to reported work [24].

3.2.2. Procedure for the preparation of 8, (dppe)PtMeI. A solution of [PtRu_2(CO)$_8$(dppe)] (208 mg, 0.204 mM) was added to methyl iodide (30 mg, 0.211 mM) in dichloromethane (10 mL), and the mixture was stirred at room temperature for 6 h. The color change was to yellow from orange–red. The solvent was removed in vacuo and the remaining solid was recrystallized from hexane/CH_2Cl_2 (5:1) at *T* = 0 °C to obtain a pale yellow crystalline solid. Yield: 88 mg (59%). m.p. 269–272 °C, Anal. Calcd for $C_{27}H_{27}P_2PtI$: C, 44.09; H, 3.70. Found: C, 44.12; H, 3.74. ^{1}H NMR: δ 6.76–7.82 (m, 20H, Ph), 1.13 (s, 3H, Pt-CH_3, $J_{Pt\text{-}H}$ = 13.84 Hz), 1.82–2.16 (m, 4H, CH_2 and P-CH_2), ^{13}C NMR: δ –5.52 (Pt-CH_3), 21.2 (P-CH_2*CH_2*), 32.6 (P-*CH_2*CH_2), 123.2–138.4 (Ph), ^{31}P NMR: δ 45.21, 45.82 and 48.06, 48.32 (two doublets, $J_{Pt\text{-}p}$ = 1628 and 3918 Hz). MS (FAB, *m/z*) = [(dppe)PtI]$^+$ (*m/z* = 719.9), [(dppe)PtCH_3]$^+$ (*m/z* = 608.1), and [Pt(dppe)]$^+$ (*m/z* = 593.1).

3.2.3. Procedure for the preparation of 9, (dppp)PtI_2. A solution of [PtRu_2(CO)$_8$(dppp)] (226 mg, 0.219 mM) and iodine (56 mg, 0.2204 mM) in dichloromethane (10 mL) was stirred at room temperature for 6 h. The color change was to yellow from orange–red. Yield: 136 mg (72%). m.p. > 300 °C, Anal. Calcd for $C_{27}H_{26}P_2PtI_2$: C, 37.65; H, 3.04. Found: C, 37.69; H, 3.06. ^{1}H NMR: δ 7.04–7.96 (m, 20H, Ph), 2.24–2.28 (m, 6H, CH_2 and P-CH_2), ^{13}C NMR: δ 20.8 (P-CH_2*CH_2*), 31.2 (P-*CH_2*CH_2), 124.0–138.6 (Ph), ^{31}P NMR: δ –10.04 ($J_{Pt\text{-}p}$ = 3660 Hz). MS (FAB, *m/z*) = [(dppp)PtI]$^+$ (*m/z* = 733.7), (dppp)Pt$^+$ (*m/z* = 605.8), and PtI_2 (*m/z* = 448).

3.2.4. Procedure for the preparation of 11, (dppp)PtRu_2(CO)$_6$(μ_3-η^2-PhC≡CPh). A solution of [PtRu_2(CO)$_8$(dppp)] (0.314 mg, 0.3037 mM) in 10 mL toluene was added to a solution of 162 mg of diphenylacetylene (0.9108 mM) in 15 mL of toluene. The mixture was heated under reduced pressure in a sealed flask for 6 h at 100 °C for 4 h. The color changed to dark red. After cooling, the solvent was removed by rotary evaporation, and the residue was separated by a silica gel column using a solvent mixture *i.e.* *n*-hexane-dichloromethane (1:1). The yield of **12** is 224 mg (63.9%) and traces of unreacted PtRu_2(CO)$_8$(dppp) (3%) were recovered. Anal. Calcd for $C_{47}H_{36}O_6P_2PtRu_2$: C, 48.83; H, 3.14. Found: C, 48.91; H, 3.18; Infrared absorption bands (CH_2Cl_2, cm^{-1}): 2048 (s), 2016 (vs), 1979 (s), 1966 (m), 1949 (m). ^{1}H NMR: δ 7.16–8.22 (m, 30H, Ph), 2.15–2.38 (m, 6H, CH_2 and P-CH_2), ^{13}C NMR: δ 22.4 (P-CH_2*CH_2*), 35.4 (P-*CH_2*CH_2), 122.0–142.6 (Ph), ^{31}P NMR: δ 10.4 (s, $J_{Pt\text{-}p}$ = 4725 Hz). MS (FAB, *m/z*) = 1155.94 [M]$^+$; [M-DPA]$^+$ 977.90; [(dppp)Pt]$^+$ 607.10.

3.2.5. Procedure for the preparation of 12, (dppe)PtRu_2(CO)$_6$(μ_3-η^2-PhC≡CPh). A 135 mg amount of PtRu_2(CO)$_8$(dppe) (0.13 mM) was mixed with 60 mg of diphenyl acetylene (0.34 mM) in 15 mL of toluene. The solution was then heated under reduced pressure at 100 °C for 4 h. The color of the solution changed from orange to dark red. The same procedure described above was used to isolate the product. The yield of the product is 108 mg of **12** (72%) and traces of unreacted $PtRu_2(CO)_8(dppe)$ (5%) were recovered. m.p. 126–28 °C, Anal. Calcd for $C_{46}H_{34}O_6P_2PtRu_2$: C, 48.38; H, 3.00. Found: C, 48.42; H, 2.96. Infrared absorption bands (CH_2Cl_2, cm^{-1}): 2048 (s), 2016 (vs), 1979 (s), 1966 (m), 1949 (m). ^1H NMR: δ 6.78–7.62 (m, 30H, Ph), 2.20–2.46 (m, 4H, CH_2 and P-CH_2 with $^2J_{P\text{-}H} = 15.3$ Hz), ^{13}C NMR: δ 22.3 (P-CH_2), 122.3–136.1 (Ph), ^{31}P NMR: δ 65.2 (s, $J_{Pt\text{-}p} = 4730$ Hz). MS (FAB, *m/z*) = 1143 $[M]^+$; $[M\text{-}DPA]^+$ 963.88; $[(dppe)Pt]^+$ 593.20. The spectroscopic data of **12** agree with the literature reported [21].

3.2.6. Procedure for the hydrogenation reaction of (dppe)PtRu$_2$(CO)$_6$(μ_3-η^2-PhC≡CPh).

A solution of $(dppe)PtRu_2(CO)_6(PhC{\equiv}CPh)$ (156 mg, 0.1359 mM) in CH_2Cl_2 had H_2 gas purged slowly through the solution at 25 °C for 10 min. Then, the flask was fitted with a balloon containing hydrogen gas (1 bar pressure) for 24 h. The color changed from orange–red to dark brown. The solvent was removed by rotary evaporation and the residue was separated by a column using a CH_2Cl_2/hexane (1:1) solvent mixture. The yield of dark orange–red product was 26 mg, identified as **13**. Along with this, other products were identified as $[(dppe)PtCl_2]$ and $Ru_3(CO)_{12}$. Anal. Calcd for $C_{56}H_{48}O_4P_4Pt_2Ru$: C, 48.03; H, 3.46. Found: C, 48.02; H, 3.48. Infrared absorption bands (CH_2Cl_2, cm^{-1}): 2050 (s), 1995 (sh), 1980 (s), 1966 (sh). ^1H NMR: δ 6.72–7.54 (m, 40H, Ph), 2.20–2.46 (m, 8H, P-CH_2), ^{13}C NMR: δ 33.4 (P-CH_2), 122.0–136.1 (Ph), ^{31}P NMR: δ 46.2 (s, $J_{Pt\text{-}p} = 4730$ Hz). MS (FAB, *m/z*) = $[M\text{-}dppe]^+ = 1029.74$; $[(dppe)PtRu(CO)_4]^+ = 806.61$; $[(dppe)PtRu(CO)_3]^+ = 777.99$; $[(dppe)PtRu(CO)_2]^+ = 750.59$; $[(dppe)PtRu(CO)_2]^+ = 722.58$; $[(dppe)Pt]^+ = 593.10$.

4. Conclusion

Platinum-based heterobimetallic carbonyl clusters, $\{L_2PtRu_2(CO)_8\}$, undergo oxidative addition reactions with methyl iodide to yield L_2PtMeI and the iodination reaction gives L_2PtI_2. These reactions are of fundamental importance to understand the behavior of bimetallic clusters in the presence of alkyl halides. $L_2PtRu_2(CO)_6(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)$ (L = PPh_3 or L_2 = dppe or dppp) are formed by heating $[(L_2Pt_2Ru(CO)_4]$ with diphenylacetylene. Hydrogenation of $(dppe)PtRu_2(CO)_6(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)$ yields stilbene and a new carbonyl cluster, $[(dppe)_2Pt_2Ru(CO)_4]$, possessing two platinum centers $\{Pt_2Ru\}$. These products are intermediates in the catalytic hydrogenation reactions of substituted alkynes. This work may provide more insight toward the stability of the bimetallic carbonyl clusters as catalysts for organic transformations. Further studies are under way to investigate the influence of substituents on triple bond carbons of acetylene in hydrogenation reactions.

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