Synthesis and organic group transfer of organodiplatinum complex with a 1,2-bis(diphenylphosphino)ethane ligand[1]

Nobuyuki Komine, Tomoko Ishiwata, Jun-ya Kasahara, Erino Matsumoto, Masafumi Hirano, and Sanshiro Komiya

Abstract: A series of homometallic alkyl- and phenyldinuclear complexes containing one platinum–platinum bond, (dppe)RPt–Pt(η^5-Cp)(CO) (R = Me, Et, CH_2CMe_3, Ph), have been prepared by oxidative addition of the Pt–C bond of PtR(η^5-Cp) to Pt(styrene)(dppe), and were characterized by spectroscopic methods and (or) X-ray structure analysis. The geometry at Pt with a dppe ligand is square planar, and the carbonyl and Cp ligand of the Pt(η^5-Cp)(CO) moiety lie orthogonal to the coordination plane of former platinum. Competitive organic group transfer reactions along the Pt–Pt bond in these complexes took place to give PtR(η^5-Cp)(CO) and PtR(η^1-Cp)(dppe) on thermolysis. Alkyl or aryl transfer from Pt with a dppe ligand were enhanced by addition of olefin, whereas treatment with CO and tertiary phosphine ligands causes Cp transfer from Pt(η^5-Cp)(CO).

Key words: organoplatinum–platinum complex, organic group transfer.

Résumé : On a préparé une série de complexes alkyl- et phényldinucléaires homométalliques contenant une liaison platine-platine, (dppe)RPt-Pt(η^5-Cp)(CO) (R = Me, Et, CH_2CMe_3, PH) par le biais d'une réaction d'addition oxydante de la liaison Pt-C du PtR(η^5-Cp) sur du Pt(styrène)(dppe) et on les a caractérisés par des méthodes spectroscopiques ainsi que par des analyses de structure par diffraction des rayons X. La géométrie au niveau du Pt portant un ligand dppe est plan carré et le groupement carbonyle et le ligand Cp de la portion Pt(η^5-Cp)(CO) se trouve en position orthogonale par rapport au plan de coordination du premier atome de platine. Il se produit des réactions compétitives de transfert des groupes organiques le long de la liaison Pt-Pt de ces complexes et elles conduisent à la formation de PtR(η^5-Cp)(CO) et PtR(η^5-Cp)(dppe) par thermolyse. Les transferts de groupes alkyles ou aryles à partir des dérivés de Pt portant le ligand dppe sont rendus plus fréquents par l'addition d'oléfine alors que des traitements par du CO ou des ligands phosphines tertiaires provoquent des transfert de Cp du Pt(η^5-Cp)(CO).

Mots-clés : complexe organique de platine–platine, transfert de groupe organique.

[Traduit par la Rédaction]

Introduction

The cooperative effect in multimetallic catalysis is one of the most intriguing and interesting unsolved problems at the molecular level both in homo- and heterogeneous catalyses (1). As the simplest model for active intermediates in various transition metal catalyzed reactions promoted by heterometallic catalysts, we previously reported the synthesis and some reactions of heterodinuclear organometallic complexes containing group 10 metals, having both M–R and M–M′ bonds, $L_nRM{-}M'L'_m$ (M = Pt, Pd; M′ = Mo, W, Co, Fe, Mn, Re; R = Me, Et, Ph, H, Ac, allyl; L_n = cod, dppe, bpy, phen, tmeda; L′ = η^5-Cp, CO) (2). They show unique reactions such as organic group transfer between different metal centers (2*a*, 2*c*, 2*d*, 2*e*, 2*h*, 2*k*, 2*q*), significant acceleration of β-hydrogen elimination (2*f*, 2*i*), enhanced CO insertion reactions into the Pd–C bond (2*g*, 2*l*), and regio- and stereoselective insertion reactions of thiiranes into the Pt–Mn (or –Re) bond controlled by an ancillary alkyl ligand (2*j*). On the other hand, organoplatinum- (or palladium-) cobalt complexes show catalytic activities in carbonylation of thietane (2*m*) and copolymerization of aziridine and CO (2*p*, 2*s*). Among these reactions, organic group transfer reactions attract interest as a simple model for easy σ-organic group movement on the heterometallic catalyst surface. The process is found to be essentially reversible and is regarded as reductive elimination of transition metal and organic groups at the transition metal. In most of the complexes we have investigated, an organic group on the platinum metal moves to other metals with small electronegativity. In this work, we investigated the synthesis and reaction of homometallic

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Received 3 April 2008. Accepted 20 May 2008. Published on the NRC Research Press Web site at canjchem.nrc.ca on 9 September 2008.

This paper is dedicated to Professor Richard Puddephatt for his great contributions in Organometallic Chemistry.

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[1] This article is part of a Special Issue dedicated to Professor R. Puddephatt.

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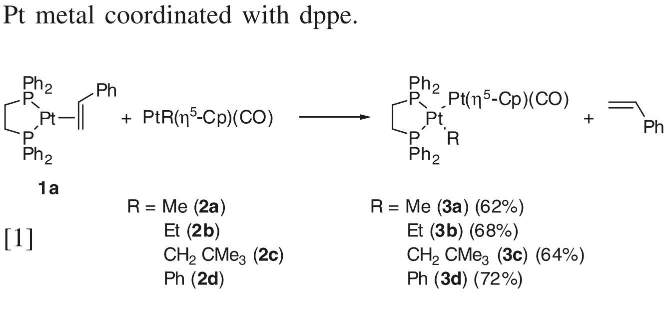
doi:10.1139/V08-111

alkyl- and aryl-dinuclear complexes containing one platinum–platinum bond (3). These complexes were synthesized by oxidative addition of the Pt–C bond of PtR(η^5-Cp)(CO) to a platinum(0) complex containing a 1,2-bis(diphenylphosphino)ethane ligand (dppe). In these dinuclear complexes, two competitive organic group transfers took place simultaneously and the reaction selectivity was controlled by additives such as olefins, carbon monoxide, and phosphine lignads.

Results and discussion

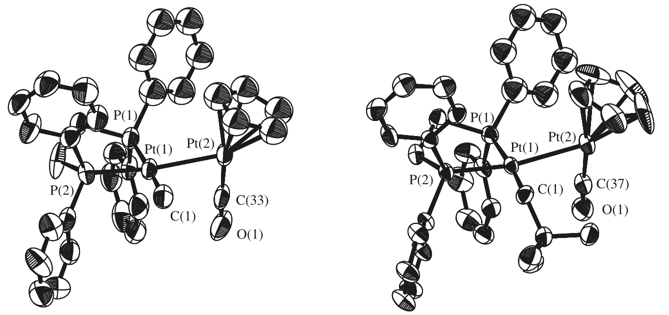
Synthesis and characterization of alkyl- (or phenyl-) platinum–platinum complexes

Treatment of the zero-valent platinum complex, Pt(η^2-CH_2=CHPh)(dppe) (**1**) with carbonyl(η^5-cyclopentadienyl)methylplatinum, PtMe(η^5-Cp)(CO) (**2a**) (4), prepared by treatment of PtMe(η^1-Cp)(cod) with CO, smoothly gave methyldiplatinum complex, (dppe)MePt–Pt(η^5-Cp)(CO) (**3a**), in 62% yield in benzene at room temperature (eq. [1]). Similar reactions with other organoplatinum complexes PtR(η^5-Cp)(CO) (R = Et (**2b**), CH_2CMe_3 (**2c**), Ph (**2d**)) also gave the corresponding organodiplatinum complexes, (dppe)RPt–Pt(η^5-Cp)(CO) (R = Et (**3b**), CH_2CMe_3 (**3c**), Ph (**3d**)). These complexes **3a**–**3d** were characterized by ^1H and $^{31}P\{^1H\}$ NMR and IR spectroscopies and elemental analysis. Single crystals of complexes **3a** and **3c** suitable for X-ray structure analysis were obtained by recrystallization from Et_2O or toluene–hexane. Figure 1 depicts an ORTEP drawing of **3a** and **3c** showing the formation of both Pt–Pt and C–Pt bonds by oxidative addition of the Pt–C bond to Pt(0). The Pt(1)–Pt(2) bond distances for **3a** and **3c** are 2.6415(10) and 2.6489(5) Å, respectively. The Pt(1)–C(1) bond distances for **3c** (2.136(9) Å) is slightly longer than for **3a** (1.98(2) Å). The geometry of the Pt metal coordinated by 1,2-bis(diphenylphosphino)ethane is essentially square planar, where the Pt(η^5-Cp)(CO) moiety and the methyl or neopentyl group are placed cis to each other. This square planar geometry is consistent with the d^8 configuration of Pt(II). The carbonyl and Cp ligands in these complexes lie orthogonal to the coordination plane of the Pt metal bearing a 1,2-bis(diphenylphosphino)ethane ligand. The Pt(2)–C(33)–O(1) [177(2)°] linkage in **3a** and Pt(2)–C(37)–O(1) [176.5(8)°] linkage in **3c** are linear compared with the corresponding linkages of heterodinuclear complexes, suggesting that these carbonyl ligands have no bridging interaction with Pt metal coordinated with dppe.



[1]

Fig. 1. Molecular structures of (dppe)MePt–Pt(η^5-Cp)(CO) (**3a**) and (dppe)(Me_3CCH_2)Pt–Pt(η^5-Cp)(CO) (**3c**). All hydrogen atoms and solvent are omitted for clarity. Elipsoids represent 50% probability. Selected bond distances (Å) for **3a**: Pt(1)–Pt(2) 2.6415(10), Pt(1)–P(1) 2.210(5), Pt(1)–P(2) 2.290(5), Pt(1)–C(1) 1.98(2), Pt(2)–C(33) 1.73(2), C(33)–O(1) 1.20(3). Selected bond angles (°) for **3a**: Pt(2)–Pt(1)–C(1) 86.8(6), P(1)–Pt(1)–P(2) 86.51(18), P(1)–Pt(1)–C(1) 91.3(7), Pt(2)–Pt(1)–P(2) 95.50(13), Pt(2)–C(33)–O(1) 177(2). Selected bond distances (Å) for **3c**: Pt(1)–Pt(2) 2.6489(5), Pt(1)–P(1) 2.221(2), Pt(1)–P(2) 2.298(2), Pt(1)–C(1) 2.136(9), Pt(2)–C(37) 1.777(10), C(37)–O(1) 1.151(12). Selected bond angles (°) for **3c**: Pt(2)–Pt(1)–C(1) 91.6(2), P(1)–Pt(1)–P(2) 85.63(8), P(1)–Pt(1)–C(1) 88.9(2), Pt(2)–Pt(1)–P(2) 93.77(6), Pt(2)–C(37)–O(1) 176.5(8).



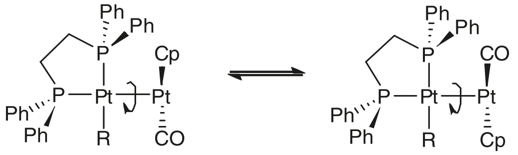
3a **3c**

The IR spectra of **3a**–**3d** show a strong ν(CO) band at ca. 1940 cm^{-1}. The value is considerably lower than that for the known Pt(II) complex PtMe(η^5-Cp)(CO) (2036 cm^{-1}) (3*a*), suggesting strong π back-donation from the Pt metal. From these data, the actual oxidation state of the Pt metal with dppe and an organic group and of the Pt metal with CO and Cp ligands were calculated to be close to two and zero, respectively, though the formal oxidation state of each is one.

The $^{31}P\{^1H\}$ NMR spectrum of **3a** shows two sets of resonances centered at δ 43.0 and 51.1, both of which are accompanied by two ^{195}Pt satellite peaks. No apparent P–P coupling is observed. The P–Pt coupling constants for the resonance at δ 43.0 (3377 and 950 Hz) are smaller than those for the resonance at δ 51.1 (1733 and 125 Hz), suggesting that the former signal is assigned to the P nucleus *trans* to the methyl ligand and the latter *trans* to Pt, since the *trans* influence of the methyl is larger than that of Pt metal (2*b*, 2*c*, 2*d*). A large second coupling constant (950 Hz) for the resonance at δ 51.1 is also consistent with the *trans* configuration between this P and Pt nuclei. $^{31}P\{^1H\}$ NMR spectra of complexes **3b**–**3d** showed similar patterns. All observations of two ^{195}Pt satellites in ^{31}P nuclei are consistent with the dinuclear structure with a Pt–Pt bond.

The ^1H NMR spectrum of **3a** in benzene-d_6 shows a double doublet with ^{195}Pt satellite for the methyl group, owing to couplings with two different P nuclei at room temperature. Cp protons in **3a** appear as a singlet at δ 5.58. The *ortho* protons of Ph in the dppe ligand are observed as two separated sets of multiplets at δ 7.7 and 7.9, each with 4H intensity. Inequivalency of the two phosphorus nuclei in dppe of **3a** is consistent with the structural result. The phenyl analogue **3d** also show similar results. On the other hand, the ethyl complex **3b** shows broad signals for the ethyl and the *ortho* protons of phenyl in the dppe ligand at room temperature. When the temperature is raised to 70 °C, clear signals consisting of a double quartet (2H) and a double triplet (3H) with Pt satellites owing to the ethyl ligand and two multiplets (4H each) for the *ortho* protons are observed. The

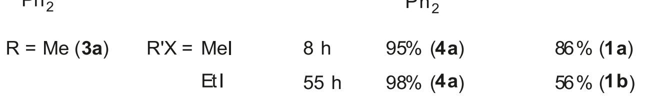
Scheme 1. Rotation of platinum–platinum bond.



results indicate that these complexes involve some fluxionality in solution without Pt–P bond rupture. When these complexes in acetone-d_6 are cooled to –40 °C, two multiplets for the *ortho* protons further split to four multiplets with 2H intensity, though unfortunately the ethyl signals are not well resolved. The result suggests that four aryl groups in dppe become magnetically inequivalent at low temperature. Such a situation becomes more clear for the ^{1}H NMR of neopentyl derivative **3c**: four separated *ortho* protons are observed at room temperature. Furthermore, methylene signals owing to the neopentyl group appear as an AB quartet that further splits into double doublets by coupling with two P nuclei with Pt satellites. Observation of the diastereotopic methylene signals indicates that **3c** is stereochemically rigid as shown by X-ray structure analysis, where CO and Cp ligands are fixed above and below the square planar coordination plane of Pt metal with dppe ligand. Therefore the observed fluxionality in **3a** and **3b** is considered to be due to the rotation of the Pt–Pt bond without any bond dissociation (Scheme 1). The qualitative ease of the Pt–Pt bond rotation decreases in the order **3a**≈**3d** > **3b** > **3c**, reflecting the increase of steric bulkiness of the alkyl ligands. The importance of steric bulk in the dinuclear system is also previously reported in the structural study of alkyl, acyl, and hydrido heterodinuclear complexes (2*r*).

To clarify the polarization of the platinum–platinum bond, reactions of methyl and ethylplatinum–platinum complexes with an electrophile were investigated (eq. [2]). The reaction of methylplatinum–platinum complex **3a** with methyl iodide in acetone-d_6 gave PtMe(η^5-Cp)(CO) (**1a**, 86%) and PtMeI(dppe) (**4a**, 95%) but no PtI(η^5-Cp)(CO) or PtMe$_2$(dppe) (eq. [2]). A similar result was obtained for the reaction of **3a** with EtI and **3b** with MeI. These results indicate that Pt with dppe is essentially electrophilic and Pt with CO is nucleophilic in both cases, being consistent with Pt(II)–Pt(0) formalism, and also with IR and X-ray structural data.

[2]

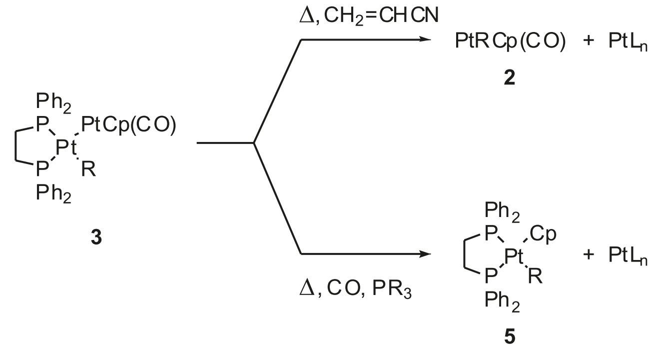


R = Me (**3a**)	R'X = MeI	8 h	95% (**4a**)	86% (**1a**)
	EtI	55 h	98% (**4a**)	56% (**1b**)
Et (**3b**)	MeI	25 h	96% (**4b**)	80% (**1a**)

Controlled organic group transfer along the platinum–platinum bond

Thermolysis of 3a–3d

Scheme 2. Controlled organic group transfer along platinum–platinum bond.



Thermolysis of organodiplatinum complexes **3a**–**3d** (Scheme 2) was carried out and the results are summarized in Table 1. Heating of methyl complex **3a** in C$_6$D$_6$ at 70 °C led to the migration of the Cp ligand to the other Pt atom giving PtMe(η^1-Cp)(dppe) (**5a**) in 55% yield with a small amount of PtMe(η^5-Cp)(CO) (**2a**) (Table 1, entry 1). The progress of the thermolysis of **3a** monitored by ^{1}H NMR indicated that **2a** and **5a** were formed simultaneously in the same ratio. Thermolysis of ethyl complex **3b** at 70 °C also gave PtEt(η^1-Cp)(dppe) (30%) accompanied by the evolution of ethylene (59%) (entry 2). Only a trace of **2b** was detected. In contrast, heating of neopentyl derivative **3c** in C$_6$D$_6$ at 70 °C led to the migration of the neopentyl ligand to the other Pt atom giving Pt(CH$_2$CMe$_3$)(η^5-Cp)(CO) (**2c**) (Table 1, entry 3) preferentially. Phenyl derivative **3d** was relatively stable and when thermolysis of **3d** was performed under similar conditions, PtPh(η^1-Cp)(dppe) (**5d**) was formed in lower yield and no **2d** was detected (entry 4). These results show that reductive elimination occurs at both Pt metals giving PtR(η^5-Cp)(CO) and PtR(η^1-Cp)(dppe). **3c** favors the organic transfer from square planar Pt but Cp ligand selectively moves to square planar Pt in the cases of **3a**, **3b**, and **3d**. In other words, reductive elimination at square planer Pt is preferred for the former, but that of Pt and Cp at the Pt(CO) site for the latter. These results are in sharp contrast with the previously reported thermal reductive elimination of the alkyl or aryl and transition metal at Pt in L$_2$RPt–M(η^5-Cp)L$_n$ giving only MR(η^5-Cp)L$_n$ (2*a*, 2*c*, 2*d*, 2*e*), in which β-hydrogen elimination of ethylplatinum–molybdenum (or –tungsten) complexes (2*d*, 2*i*) and no Cp transfer were observed. Unfortunately, corresponding Pt(0) products were not identified. The stronger electron-donating property of the neopentyl ligand may accelerate the reductive elimination (5). The origin of the present selectivity difference of organic group transfer is not clear at present and further detailed kinetic and theoretical studies are required.

Organic group transfer assisted by olefins, carbon monoxide, or phosphine ligands

When the organodiplatinum complexes **3a**–**3d** were treated with olefins, CO, and tertiary phosphine ligands, organic transfer reactions were enhanced. Results of the reactions at room temperature are also summarized in Table 1.

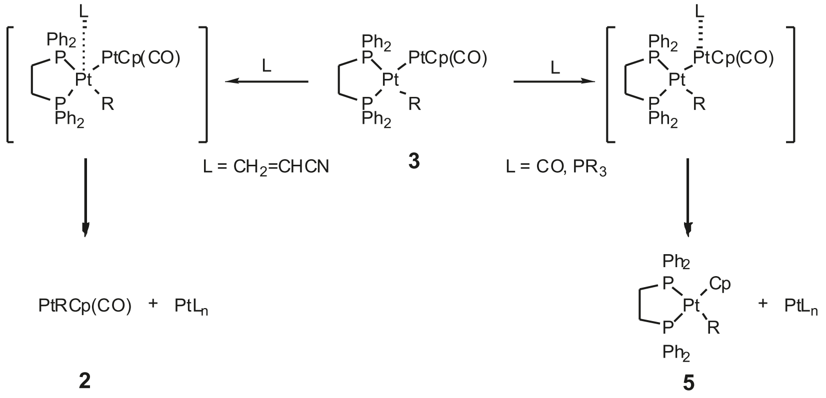
Treatment of **3a** with 5 equiv. of acrylonitrile in C$_6$D$_6$ gave **2a** (35%) and **5a** (19%) in 2 h, showing acceleration of methyl transfer at the square planar platinum site (Table 1, entry 5) (6). Reaction with methyl acrylate also produced a similar result, though the rate was relatively slow (Table 1, entry 6). Styrene showed no large effect on reductive elimi-

Table 1. Organic group transfer of organoplatinum–platinum complex with a 1,2-bis(diphenylphosphino)ethane ligand.

						Yield (%)	
Entry	Complex	Additive	Temp.	Time	Conv. (%)	**2**	**5**
1	**3a**	None	70 °C	25 h	83	7	55
2[a]	**3b**	None	70 °C	25 h	92	Trace	43
3	**3c**	None	70 °C	6 h	74	47	Trace
4	**3d**	None	70 °C	24 h	53	0	18
5	**3a**	CH_2=CHCN (5 eq)	RT	2 h	65	35	19
6	**3a**	CH_2=CH(CO_2Me) (5 eq)	RT	24 h	50	21	19
7	**3a**	CH_2=CHPh (5 eq)	RT	24 h	16	2	10
8	**3b**	CH_2=CHCN (5 eq)	RT	22 h	55	37	13
9	**3c**	CH_2=CHCN (5 eq)	RT	24 h	24	15	4
10	**3d**	CH_2=CHCN (5 eq)	RT	1.5 h	56	56	1
11	**3a**	CO (1 atm)	RT	Instant	100	13	59
12	**3c**	CO (1 atm)	RT	4 h	76	20	41
13	**3d**	CO (1 atm)	RT	2 h	97	25	67
14	**3a**	dppe (5 eq)	RT	Instant	0	0	52
15	**3a**	PPh_3 (10 eq)	RT	Instant	2	0	94

Note: Reactions were performed in C_6D_6.
[a]Evolution of ethylene (59%).

Scheme 3. A possible mechanism for controlled organic group transfer along platinum–platinum bond.



nation (Table 1, entry 7). A similar trend was also observed in the reactions of **3b** and **3d** (Table 1, entries 8 and 10). No significant effect was observed for the neopentyl derivative **3c** (Table 1, entry 9). These results can be reasonably understood by the coordination of these substituted olefins to the square planar platinum atom enhancing the reductive elimination of PtR(η^5-Cp)(CO) complexes, similar to the organic transfer of heterodinuclear organoplatinum complexes assisted by electron deficient olefins, which was previously reported by us (2*a*, 2*c*, 2*d*, 2*e*). Coordination of electron-deficient olefins to the square planar platinum complexes enhances the reductive elimination. Therefore the relatively electron-rich styrene showed no significant effect. The low acceleration by added acrylonitrile to the neopentyl complex **3c** could be due to the fact that the sterically bulky neopentyl ligand discourages coordination. The importance of steric bulkiness of the neopentyl ligand is also discussed in the NMR study (vide supra).

In contrast, reaction of a C_6D_6 solution of **3a**, **3c**, **3d** with CO (1 atm) at room temperature afforded PtR(η^1-Cp)(dppe) (R = Me (**5a**), CH_2CMe_3 (**5c**), Ph (**5d**)) as the major product (Table 1, entries 11–13). When **3a** was treated with a tertiary phosphine ligand such as 1,2-bis(diphenylphosphino)ethane (dppe) or PPh_3 in C_6D_6 at room temperature, selective Cp group transfer took place to give only PtMe(η^1-Cp)(dppe) (**5a**) in high yield (Table 1, entries 14, 15).

Possible mechanism for controlled organic group transfer along platinum–platinum bond

As shown in Scheme 3, competitive organic group transfer reactions along the Pt–Pt bond in organodiplatinum complexes (dppe)RPt–Pt(η^5-Cp)(CO) take place to give PtR(η^5-Cp)(CO) and PtR(η^1-Cp)(dppe) on thermolysis. The reaction was enhanced by the coordination of additives such as olefin, CO, and tertiary phosphine ligands. The selectivity of the reaction is affected by the coordination site of the added substrate. Specifically, the organic group transfer at square planar platinum is favored by interaction with electron-deficient olefin, whereas Cp group transfer from Pt(η^5-Cp)(CO) to PtR(dppe) is enhanced by tertiary phosphine ligands or carbon monoxide. Probably, these ligands favor the coordination at the Pt(η^5-Cp)(CO) site to enhance the Cp migration, while preferred coordination of π-accepting ligands such as acrylonitrile to the Pt metal with an electron-donating dppe ligand gives PtR(η^5-Cp)(CO). The acceleration effect of added olefin on the alkyl transfer reaction is well established in the reductive elimination of square planar diorganonickel (or palladium) complexes (7) and heterodinuclear organometallic complexes containing platinum (2*a*, 2*c*, 2*d*). The observed selective reaction caused by ligands could be due to the thermodynamic stability of products. For example, reductive elimination at the (dppe)Pt site favors Pt(0) product such as Pt(olefin)(dppe) rather than a putative complex Pt(olefin)$(CO)_n$ with ligands with all strong π-back-donation. Further detailed study including a theoretical approach is required to clarify the origin of this selectivity.

Experimental

General

All manipulations were carried out under dry nitrogen or argon atmosphere using standard Schlenk and vacuum line techniques. Solvents (benzene, toluene, hexane, and THF) were refluxed over and distilled from sodium benzophenone ketyl under N_2. Deuterated solvents were degassed by three freeze-pump-thaw cycles and then vacuum-transferred from appropriate drying agents (C_6D_6 from sodium wire, acetone-d_6 from drierite). The zero-valent platinum complex, Pt(η^2-CH_2=CHPh)(dppe) was prepared by the reaction of PtI_2(dppe) with $NaBH_4$ in the presence of a large excess of the styrene according to the analogous literature method (2*k*). PtR(η^1-Cp)(cod) were prepared by the reaction of PtRCl(cod) and NaCp according to the analogous literature methods with modifications (3). PtR(η^1-Cp)(dppe) (R = Me (**5a**), Et (**5b**), CH_2CMe_3 (**5d**), Ph (**5e**)) were prepared for assignment, according to the analogous literature methods (8). NMR spectra were recorded on a JEOL LA-300 spectrometer (300.4 MHz for ^{1}H, 121.6 MHz for ^{31}P). Chemical shifts were reported in ppm downfield from TMS for ^{1}H and from 85% H_3PO_4 in D_2O for ^{31}P. IR spectra were recorded on a JASCO FT–IR-410 spectrometer using KBr disks. Elemental analyses were carried out with a Perkin-Elmer 2400 series II CHN analyzer.

Synthesis of organoplatinum–platinum complexes

As a typical procedure, the oxidative addition of methyl(η^5-cyclopentadienyl)(monocarbonyl)platinum complex (**2a**) to the zero-valent platinum complex, Pt(η^2-CH_2=CHPh)(dppe) (**1**) to afford (dppe)MePt–Pt(η^5-Cp)(CO) (**3a**) is described. PtMe(η^5-Cp)(CO) was first prepared by treating PtMe(η^1-Cp)(cod) (69.9 mg, 0.169 mmol) with CO and dissolving it in benzene (3 mL). This was then added to a solution of Pt(η^2-CH_2=CHPh)(dppe) (105.2 mg, 0.1507 mmol) in benzene (10 mL). The reaction mixture was stirred at room temperature for 1 h. After the solution was concentrated under reduced pressure, excess hexane was added to give a yellow powder. The product was filtered, washed with hexane, and dried under vacuum at room temperature. Recrystallization from ether gave yellow crystals (yield: 62%). IR (KBr, cm^{-1}) ν(CO): 1933. ^{1}H NMR (C_6D_6, RT, 300.4 MHz) δ: 1.6–1.8 (m, 4H, dppe C*H*$_2$), 1.80 (dd, $^3J_{PH}$ = 7.4, 5.1 Hz, $^2J_{PtH}$ = 64.9 Hz, 3H, PtC*H*$_3$), 5.58 (m, 5H, *Cp*), 6.8–7.3 (m, 12H, *m,p-Ph*), 7.66 (m, 4H, *o-Ph*), 7.80 (m, 4H, *o-Ph*). ^{1}H NMR (acetone-d_6, RT, 300.4 MHz) δ: 1.01 (dd, $^3J_{PH}$ = 7.6, 4.9 Hz, $^2J_{PtH}$ = 66.4 Hz, 3H, PtC*H*$_3$), 2.15–2.42 (m, 4H, dppe C*H*$_2$), 5.25 (m, 5H, *Cp*), 7.40–7.65 (m, 12H, *m,p-Ph*), 7.70–7.95 (m, 8H, *o-Ph*). ^{31}P{^{1}H} NMR (C_6D_6, RT, 121.6 MHz) δ: 41.7 (s, $^1J_{PtP}$ = 3289 Hz, $^2J_{PtP}$ = 1010 Hz), 51.7 (s, $^1J_{PtP}$ = 1702 Hz, $^2J_{PtP}$ = 132 Hz). ^{31}P{^{1}H} NMR (acetone-d_6, RT, 121.6 MHz) δ: 43.0 (s, $^1J_{PtP}$ = 3377 Hz, $^2J_{PtP}$ = 950 Hz), 51.1 (s, $^1J_{PtP}$ = 1733 Hz, $^2J_{PtP}$ = 125 Hz). Anal. calcd. for $C_{39}H_{38}OP_2Pt_2$: C 48.05, H 3.93; found: C 47.69, H 3.99.

(dppe)EtPt–Pt(η^5-Cp)(CO) (3b)

140.3 mg (0.1372 mmol, 73%). IR (KBr, cm^{-1}) ν(CO): 1934. ^{1}H NMR (C_6D_6, 70 °C, 300.4 MHz) δ: 1.55–2.00 (m, 4H, dppe C*H*$_2$), 1.56 (dt, $^3J_{PtH}$ = 45.6 Hz, $^2J_{HP}$ = 10.8 Hz, $^3J_{HH}$ = 7.8 Hz, 3H, PtCH$_2$C*H*$_3$), 2.62 (dq, $^2J_{PtH}$ = 71.5 Hz, $^2J_{PH}$ = 14.7 Hz, $^2J_{HH}$ = 7.2 Hz, 2H, PtC*H*$_2$CH$_3$), 5.61 (m, 5H, *Cp*), 7.02–7.23 (m, 12H, *m,p-Ph*), 7.60–7.87 (m, 8H, *o*-Ph). ^{31}P{^{1}H} NMR (C_6D_6, 70 °C, 121.6 MHz) δ: 42.0 (s, $^1J_{PtP}$ = 3453 Hz, $^2J_{PtP}$ = 977 Hz, $^3J_{PP}$ = 3.6 Hz), 49.3 (s, $^1J_{PtP}$ = 1480 Hz, $^2J_{PtP}$ = 141 Hz, $^3J_{PP}$ = 3.6 Hz). Anal. calcd. for $C_{41}H_{42}OP_2Pt_2$: C 48.72, H 3.79; found: C 49.10, H 4.22.

(dppe)(Me_3CCH_2)Pt–Pt(η^5-Cp)(CO) (3c)

106.5 mg (0.1119 mmol, 64%). IR (KBr, cm^{-1}) ν(CO): 1941. ^{1}H NMR (C_6D_6, RT, 300.4 MHz) δ: 1.28 (s, 9H, CH$_2$C*Me*$_3$), 1.4–1.9 (m, 4H, dppe C*H*$_2$), 2.75 (td, $^2J_{HH}$ = $^3J_{PH}$ = 11.7 Hz, $^3J_{PH}$ = 8.4 Hz, $^2J_{PtH}$ = 52.3 Hz, 1H, C*H*$_2$CMe$_3$), 2.92 (ddd, $^2J_{HH}$ = 11.7 Hz, $^3J_{PH}$ = 7.8, 3.3 Hz, $^2J_{PtH}$ = 72.7 Hz, 1H, C*H*$_2$CMe$_3$), 5.56 (m, 5H, *Cp*), 7.0–7.2 (m, 12H, *m*, *p*-Ph), 7.53 (m, 2H, *o*-Ph), 7.63 (m, 2H, *o*-Ph), 7.70 (m, 2H, *o*-Ph), 7.79 (m, 2H, *o*-Ph). ^{31}P{^{1}H} NMR (C_6D_6, RT, 121.6 MHz) δ: 40.7 (d, $^1J_{PtP}$ = 3408 Hz, $^2J_{PtP}$ = 1860 Hz, $^2J_{PP}$ = 3.6 Hz), 50.8 (d, $^1J_{PtP}$ = 1508 Hz, $^2J_{PtP}$ = 175 Hz, $^2J_{PP}$ = 3.6 Hz).

(dppe)PhPt–Pt(η^5-Cp)(CO) (3d)

49.9 g (0.052 mmol, 31%). IR (KBr, cm^{-1}) ν(CO): 1947. ^{1}H NMR (C_6D_6, RT, 300.4 MHz) δ: 1.6–1.8 (m, 4H, dppe C*H*$_2$), 5.42 (m, 5H, *Cp*), 6.9–7.3 (m, 15H, *m,p*-Ph, dppe *m*, *p*-Ph), 7.47 (m, 4H, dppe *o*-Ph), 7.68 (t, $^3J_{HH}$ = $^3J_{PH}$ = 7.1 Hz, $^3J_{PtH}$= 45.7 Hz, 2H, *o*-Ph), 7.96 (m, 4H, dppe *o*-Ph). ^{1}H NMR (acetone-d_6, RT, 300.4 MHz) δ: 2.15–2.42 (m, 4H, dppe C*H*$_2$), 5.61 (m, 5H, *Cp*), 6.45 (t, $^3J_{HH}$ = 7.4 Hz, 1H, *p*-Ph), 6.67 (td, J_{HH} = 7.4, 1.7 Hz, 2H, *m*-Ph), 7.11 (td, $^3J_{HH}$ = $^3J_{PH}$ = 7.4 Hz, $^3J_{HH}$ = 1.7 Hz, $^3J_{PtH}$= 45.4 Hz, 2H, *o*-Ph), 7.54–7.62 (m, 16H, dppe *o,m,p*-Ph), 7.90–8.05 (m, 4H, dppe *o*-Ph). ^{31}P{^{1}H} NMR (C_6D_6, RT, 121.6 MHz) δ: 37.4 (s, $^1J_{PtP}$ = 3185 Hz, $^2J_{PtP}$ = 995 Hz), 48.2 (s, $^1J_{PtP}$ = 1645 Hz, $^2J_{PtP}$ = 127 Hz). ^{31}P{^{1}H} NMR (acetone-d_6, RT, 121.6 MHz) δ: 43.0 (s, $^1J_{PtP}$ = 3272 Hz, $^2J_{PtP}$ = 960 Hz), 47.6 (s, $^1J_{PtP}$ = 1655 Hz, $^2J_{PtP}$ = 127 Hz).

Reactions with alkyl halide

A typical procedure for **3a** with methyl iodide in acetone-d_6 is given. Acetone-d_6 (0.5 mL) was vacuum-transferred to an NMR tube (5 mmϕ × 180 mm) containing **3a** (5.3 mg, 5.9 × 10^{-3} mmol), and 1,4-dioxane was added as an internal standard to the solution. Then 1 equivalent of methyl iodide was introduced into the NMR tube. NMR spectra were periodically measured to follow the reactions. Results are summarized in Table 1.

Thermolysis

A typical procedure for **3a** in C_6D_6 is given. C_6D_6 (0.5 mL) was vacuum-transferred to an NMR tube containing **3a**, and 1,4-dioxane was added as an internal standard to the solution. Then the NMR tube was heated on oil bath. NMR spectra were periodically measured to follow the reactions. Results are summarized in Table 1.

Reactions with olefin or phosphine ligand

A typical procedure for **3a** in C_6D_6 is given. C_6D_6 (0.5 mL) was vacuum-transferred to an NMR tube containing **3a**, and 1,4-dioxane was added as an internal standard to the solution. Then olefin or phosphine ligand was introduced into the NMR tube. NMR spectra were periodically measured to follow the reactions. Results are summarized in Table 1.

Reactions with CO

A typical procedure for **3a** is given. C_6D_6 (0.5 mL) was vacuum-transferred to an NMR tube containing **3a**, and 1,4-dioxane was added as an internal standard to the solution. The solution was degassed by freeze-pump-thaw cycles and CO (0.1 MPa) was introduced. NMR spectra were periodically measured to follow the reaction. Results are summarized in Table 1.

X-ray structure data[3]

The crystallographic data were measured on a Rigaku RASA-7R four-circle diffractometer using Mo Kα (λ = 0.710 69 Å) radiation with a graphite crystal monochromator at –73 °C. A single crystal was selected by means of a polarized microscope and mounted in a capillary tube (GLASS, 0.7 mmϕ), which was sealed by small flame torch, or onto a glass capillary with Paraton N oil. The unit cell dimensions were obtained by a least-squares fit of 20 centered reflections. Intensity data were collected using the ω-2θ technique to a maximum 2θ of 55.0°. The scan rates were 16.0 deg/min. Three standard reflections were monitored in every 150 reflections. Intensities were corrected for Lorentz and polarization effects. The data were processed using the Crystal Structure (9, 10) crystallographic software package. The structure of **3a** and **3c** was solved by Patterson methods (DIRDIF99 PATTY). An absorption correction for **3c** was applied with the program PSI SCAN method. All non-hydrogen atoms were found on difference maps.

(dppe)MePt–Pt(η^5-Cp)(CO) (3a)

For complex **3a**, all non-hydrogen atoms were refined with anisotropic displacement parameters except for one of the phenyl rings of dppe, Cp ring atoms, and the incorporated solvent molecule, which were treated as a fixed group. Crystallographic data: **3a**·Et_2O: $C_{37}H_{42}O_2P_2Pt_2$, FW: 970.83, triclinic. $P1$ (No. 2) a: 11.952(7) Å, b: 18.217(16) Å, c: 8.955(2) Å, α: 101.24(5)°, β: 99.72(3)°, γ: 71.37(7)°. V: 1800.1(19) Å^3. Z: 2. D_{calcd}: 1.791 g cm^{-3}. 5356 unique reflections with $I > 3\sigma(I)$. R_1: 0.080, wR_2: 0.099.

(dppe)(Me_3CCH_2)Pt–Pt(η^5-Cp)(CO) (3c)

For complex **3c**, all non-hydrogen atoms were refined with anisotropic displacement parameters except for one of the phenyl rings of dppe and the incorporated solvent molecule. The solvent molecule was refined with isotropic displacement parameters, and one phenyl ring of dppe was treated as a fixed group. Crystallographic data: **3c**·$2C_6H_6$: $C_{49}H_{52}OP_2Pt_2$, FW: 1109.08, monoclinic. $P2_1/n$ (No. 14) a: 11.61(7) Å, b: 20.43(9) Å, c: 18.67(6) Å, β = 91.8(3)°. V: 4425.1(346) Å^3. Z: 4, D_{calcd}: = 1.665 g·cm^{-3}. 7679 unique reflections with $I > 3\sigma(I)$. R_1: 0.0462, wR_2: 0.0622.

Acknowledgement

This work was financially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Sports, Culture, Science, and Technology, Japan.

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[3] Supplementary data for this article are available on the journal Web site (canjchem.nrc.ca) or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0R6, Canada. DUD 3798. For more information on obtaining material refer to cisti-icist.nrc-cnrc.gc.ca/cms/unpub_e.shtml. CCDC 683196 and 683197 contain the crystallographic data for this manuscript. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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