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Mono- and Diphosphine Platinum(0) Complexes of Methylenecyclopropane, Bicyclopropylidene, and Allylidenecyclopropane

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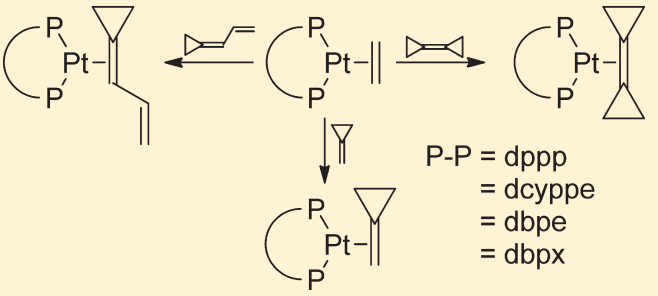
Supporting Information

ABSTRACT: The syntheses of the first platinum complexes with η^2-bicyclopropylidene ligands are reported herein. Complexes of the formula [Pt(L)(P−P)] (L = η^2-bicyclopropylidene, η^2-methylenecyclopropane, P−P = $Ph_2P(CH_2)_3PPh_2$, $Cyp_2P(CH_2)_2PCyp_2$, $^tBu_2P(CH_2)_2P^tBu_2$, $^tBu_2PCH_2(o\text{-}C_6H_4)\text{-}CH_2P^tBu_2$) were synthesized by addition of the free alkene to ethene precursor complexes. Bicyclopropylidene underwent a ring-opening reaction with both Pt(0) and Pt(II) complexes to form allylidenecyclopropane, and the first allylidenecyclopropane complexes were synthesized, some of which underwent a rearrangement to form η^2:σ^2-metallacyclo-3-pentene complexes. Mixed alkene complexes [Pt(C_2H_4)(L)(PR_3)] (L = η^2-bicyclopropylidene, η^2-methylenecyclopropane, PR_3 = PPh_3, PCy_3) and bis-methylenecyclopropane complexes [Pt(MCP)$_2$(PR_3)] (PR_3 = PPh_3, PCy_3) were synthesized by the addition of the free alkene to bis-ethene precursors.



INTRODUCTION

Bicyclopropylidene (BCP) and methylenecyclopropane (MCP) belong to a class of alkenes that contain cyclopropyl rings with exocyclic double bonds. These alkenes have a rich chemistry and are active toward transition metal catalysts, particularly those of the group 10 metals.[1−4] However, the isolation of transition metal complexes containing these alkenes in η^2-coordination has not received as much focus as their reactivity. Only a handful of η^2-MCP complexes have been reported to date,[5−8] while there have been just two of η^2-BCP, both of first-row transition metals.[7,8] A better understanding of the coordination chemistry of these interesting alkenes could provide valuable insight into their reactivity patterns. Despite the lack of isolated complexes, MCP and BCP are expected to be good ligands toward transition metals, with their high-lying HOMOs capable of effectively donating electron density into empty metal orbitals,[2,7] while alleviation of strain in the highly strained cyclopropyl rings upon coordination is a strong driving force for the formation of stable complexes. As platinum(0) is a strong π-donor, capable of effective back-donation, it is ideal for making the first late transition metal complexes of BCP. The successful synthesis of the Pt(0) complex [Pt(MCP)(PPh_3)$_2$] is a strong indication of the viability of such complexes.[5]

RESULTS AND DISCUSSION

[Pt(L)(P−P)] Complexes. A range of Pt(0) complexes containing chelating diphosphine auxiliary ligands were used as precursors. These complexes were chosen because chelating phosphines not only stabilize transition metal complexes, but also allow the coordination of only one alkene ligand, thus preventing possible oligomerization reactions. The diphosphines used in this research were 1,3-bis(diphenylphosphino)propane (dppp), 1,2-bis(dicyclopentylphosphino)ethane (dcyppe), 1,2-bis[(di-*tert*-butylphosphino)methyl]benzene (dbpx), and 1,2-bis(di-*tert*-butylphosphino)ethane (dbpe). Ethene complexes were chosen as suitable precursors due to the ease of displacement of the ethene ligand and the simplicity of the NMR spectra of both the free and coordinated ethene, which facilitates the monitoring of the reactions. A range of methods were used to synthesize the various ethene complexes, the choice of method dictated by the diphosphine ligand. The complexes [Pt(C_2H_4)(dbpx)] and [Pt(C_2H_4)(dbpe)] were synthesized by adding the diphosphine to [Pt(C_2H_4)$_3$], generated *in situ* from [Pt(1,5-cyclooctadiene)$_2$] ([Pt(COD)$_2$]).[9] This method was unsuitable for the synthesis of [Pt(C_2H_4)(dppp)], as the coordination of a second dppp ligand to form [Pt(dppp)$_2$] is very facile. Instead, the ethene complex was generated by the reduction of [$PtCl_2$-(dppp)] under an ethene atmosphere using $NaBH_4$. While the reaction of dcyppe with [Pt(C_2H_4)$_3$] yielded [Pt(C_2H_4)(dycppe)], problems with purification meant that this was not a viable synthesis method. The $NaBH_4$ method was attempted, but was not successful. Instead, [Pt(C_2H_4)(dycppe)] was synthesized by the reduction of [$PtCl_2$(dcyppe)] using sodium amalgam. Complexes of 1,

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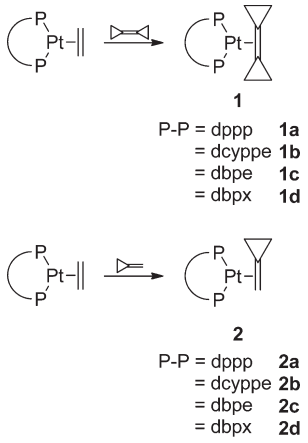
2-bis(diphenylphosphino)ethane (dppe) were considered, as these would have made a good comparison for the dppp complexes. However, $[Pt(C_2H_4)(dppe)]$ could not be synthesized from $[Pt(C_2H_4)_3]$ due to the facile formation of $[Pt(dppe)_2]$, while reduction methods yielded only $[Pt_3H_3(dppe)_3]^+$. This is because the intermediate hydride complex in the reduction is dimeric for dppe, rather than monomeric as for dppp.[10,11] While the synthesis of $[Pt(C_2H_4)(dppe)]$ using sodium naphthalenide has been reported, this method did not involve the isolation of the pure ethene complex, which meant that this synthesis was not suitable for the NMR-scale studies undertaken here.[12]

Scheme 1. Synthesis of [Pt(BCP)(P−P)] and [Pt(MCP)(P−P)]



Methylenecyclopropane was made by the reaction of methallyl chloride with sodium amide and potassium *tert*-butoxide,[13] while the synthesis of bicyclopropylidene made use of the Kulinkovich reaction to produce cyclopropylcyclopropanol, which was then converted to the bromide followed by dehydrobromination to produce the alkene.[14] BCP and MCP complexes were synthesized via the displacement of the ethene ligand from the precursor complexes. This was done by dissolving the ethene complex in either toluene or d_6-benzene and adding an excess of the appropriate alkene, producing the diphosphine complexes $[Pt(BCP)(P-P)]$ (**1**) and $[Pt(MCP)(P-P)]$ (**2**) (P−P = dppp (**a**), dcyppe (**b**), dbpe (**c**), dbpx (**d**)) (Scheme 1).

Whereas BCP is an easily handled liquid, MCP is a gas at room temperature, with a boiling point of 10 °C. For this research, it was deemed most practical to use MCP by cooling a glass syringe and then rapidly injecting a small amount of the liquid alkene into the reaction vessel. The formation rates of the complexes were dependent on both the size of the alkene and the size of the diphosphine ligand. MCP, with only one cyclopropyl ring (^{c}Pr), coordinated more rapidly than BCP, with two rings. The steric

Table 1. Selected NMR Data of [Pt(L)(P−P)][a]

compound		δ_P	$^1J_{Pt-P}$	$^2J_{P-P}$		δ_H ^{c}Pr	J_{Pt-H}	δ_H =CHR	$^2J_{Pt-H}$	δ_C ^{c}Pr	J_{Pt-C}	δ_C =CR_2	$^1J_{Pt-C}$	δ_C =CHR	$^1J_{Pt-C}$
BCP						1.18				3.33		110.61			
MCP						0.90		5.46		2.94		131.06		103.49	
ACP						0.93		6.58		2.64		129.33		136.88	
						0.85				2.28					
[Pt(BCP)(dppp)]	**1a**	9.29	2932			1.29	66.0			8.82	23.1	34.25	410.8		
						1.18	37.7								
[Pt(BCP)(dcyppe)]	**1b**	70.77	2731			1.5−1.4	[b]			10.43	23.1	33.76	424.6		
[Pt(BCP)(dbpe)]	**1c**	97.43	2798			1.57	[b]			9.89	23.7	31.77	428.9		
						1.31	[b]								
[Pt(BCP)(dbpx)]	**1d**	43.31	2983			1.34	61.2			9.87	22.5	29.27	456.3		
						0.99	32.0								
[Pt(MCP)(dppp)]	**2a**	11.73	3275	42	*trans* =CH_2	1.65	33.0	2.63	65.3	10.08	25.9	42.67	455.4	25.29	173.4
		11.35	2975		*trans* =CR_2	1.32	82.5								
[Pt(MCP)(dcyppe)]	**2b**	75.03	2751	63	*trans* =CR_2	1.95	[b]	2.40	60.5	12.30	23.0	38.25	501.0	22.35	169.0
		70.83	3107		*trans* =CH_2	1.80	[b]								
[Pt(MCP)(dbpe)]	**2c**	100.84	2807	66	*trans* =CR_2	1.89	33.6	2.39	60.6	11.82	24.5	36.81	511.4	23.54	171.6
		99.15	3167		*trans* =CH_2	1.79	60.0								
[Pt(MCP)(dbpx)]	**2d**	49.25	3362	30	*trans* =CH_2	1.60	[b]	2.12	56.2	11.41	25.0	33.61	537.6	27.83	164.2
		43.74	3025		*trans* =CR_2	1.60	[b]								
[Pt(ACP)(dppp)]	**3a**	10.34	3293	39	*trans* =CHR	1.3−0.8	[b]	3.78	67.8	[b]	[b]	[b]	[b]	[b]	[b]
		9.67	3003		*trans* =CR_2										
[Pt(ACP)(dcyppe)]	**3b**	69.97	3153	−59	*trans* =CHR	[b]	[b]	3.41	62.1	[b]	[b]	[b]	[b]	[b]	[b]
		68.60	2771		*trans* =CR_2										
[Pt(ACP)(dbpe)]	**3c**	96.40	2848	62	*trans* =CR_2	1.5	[b]	3.43	62.0	10.60	17.7	41.43	533.1	44.72	165.5
		96.39	3196		*trans* =CHR	1.0	[b]			9.47	15.5				
[Pt(C_2H_4)(dppp)]		13.76	3340					2.68	60.0					31.85	216.0
[Pt(C_2H_4)(dcyppe)]		75.44	3170					2.38	58.0					23.18	227.4
[Pt(C_2H_4)(dbpe)]		102.54	3230					2.41	59.4					24.95	229.0
[Pt(C_2H_4)(dbpx)]		50.10	3493					2.20	57.3					27.20	217.0

[a] δ values are given in ppm and J values in Hz. All spectra were measured in C_6D_6 at room temperature. [b] NMR data could not be obtained.

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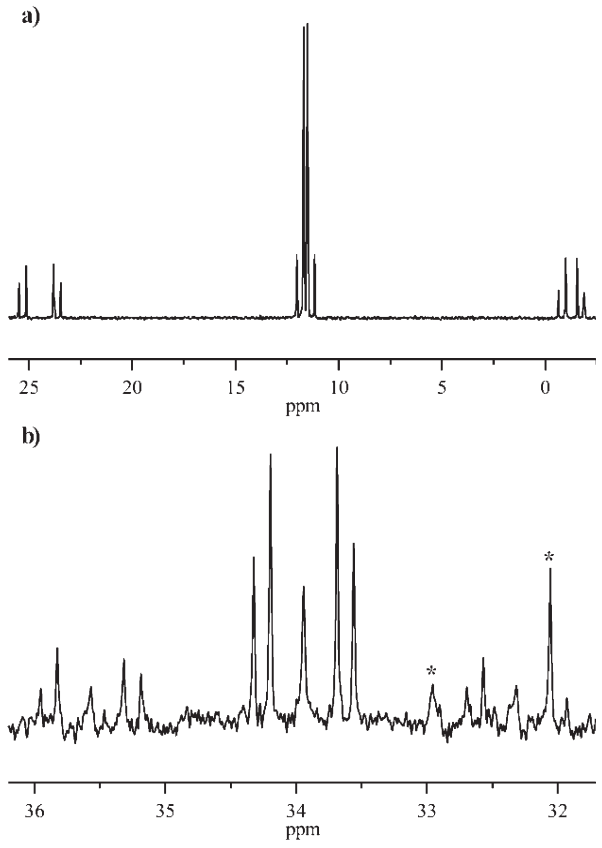

Figure 1. (a) ^{31}P NMR spectrum of **2a**. (b) ^{13}C NMR spectrum of the double-bond carbons of **1a**.

bulk of the substituents on the phosphine ligands had a more significant effect on the formation rates. Complexes of dppp formed most rapidly, with the reaction occurring almost instantly at room temperature. Complexes of dcyppe reacted more slowly, forming overnight at room temperature. Both of the ^{t}Bu phosphines required heating, overnight at 40 and 60 °C for **2c** and **2d**, respectively, and for up to 6 days at 60 °C for **1c** and **1d**. The dependence of reaction rate on steric bulk points to an associative exchange mechanism.

The magnitude of the platinum−phosphorus $^{1}J_{Pt-P}$ coupling constants in the ^{31}P NMR spectra of **1** and **2** showed that the alkenes were in η^2-coordination. In the BCP complexes, $^{1}J_{Pt-P}$ values were between 2731 and 2983 Hz (Table 1), ∼450 Hz less than those in the parent ethene complex. The ^{31}P NMR spectra of **2** had second-order ABX (A, B = ^{31}P, X = ^{195}Pt) peak patterns due to the asymmetry of the alkene and the rigid coordination geometry (Figure 1a). The $^{1}J_{Pt-P}$ values could be used to distinguish the P *trans* to the ^{c}Pr group from that of the P *trans* to the methylene in the MCP complexes, as the two coupling constants were comparable to those of **1** and the parent ethene complexes, respectively.

The ^{13}C NMR spectra also clearly showed that the alkenes were in η^2-coordination. The cyclopropyl double-bond carbons showed large $^{1}J_{Pt-C}$ values, 410−456 Hz for **1** and 455−538 Hz for **2** (Table 1), while the methylene carbon in **2** had $^{1}J_{Pt-C}$ values several hundred Hz less (164−173 Hz). There was also a large upfield shift of the ^{c}Pr double-bond carbon resonances upon coordination, from 110.6 to 29−34 ppm for **1** and from 131.0 to 33−43 ppm for **2**. The methylene carbon was typically ∼15 ppm upfield of the ^{c}Pr carbon, except for in **2d**, where the difference was only 5.8 ppm. For comparison, the methylene chemical shift differed from that of the parent ethene ligand by 0.6−6.6 ppm. A stronger Pt−C bond is formed to the cyclopropyl carbons in **1** and **2** than to the methylene carbons in **2** and the parent ethene complexes. This is evidenced by the lower $^{1}J_{Pt-P}$ of the P *trans* to the cyclopropyl carbons and the higher $^{1}J_{Pt-C}$ coupling constants of these carbons and is a result of the decrease in strain energy of the ^{c}Pr rings by rehybridization upon coordination.[15−19]

For the double-bond carbons in **1**, the line shape was characteristic of a "false AA′X" spin system (A, A′ = ^{31}P, X = ^{13}C) with ^{195}Pt satellites due to both the magnetic inequivalence of the two chemically equivalent carbons when one was ^{13}C and the two ^{31}P atoms having the same chemical shift (Figure 1b).[20,21] The double-bond carbons in **2**, however, were ABX systems with ^{195}Pt satellites, as the two ^{31}P atoms were in different chemical environments.[21] These ^{13}C NMR peaks, and the ^{31}P NMR spectra of **2**, indicate that the alkene ligands do not rotate at room temperature when coordinated, as rotation would result in the two ^{31}P atoms becoming equivalent.

X-ray quality crystals of **1a** were grown by recrystallization from toluene, and an X-ray crystal structure was obtained (Figure 2). The BCP C═C bond length increased from 1.304(2) Å in the free alkene to 1.427(3) Å in **1a**, an increase of 9.4%.[22] This was greater than the 7.4% increase observed for [Co(BCP)(η^5:η^1[2-(di-*tert*-butylphosphanyl-*P*)ethyl]cyclopentadienyl)], which had a C═C bond length of 1.401(5) Å.[8] The bond length of **1a** was closer to that of the comparable C−C bond in bicyclopropyl (1.487(4) Å, differing from **1a** by 0.06 Å) than to the C═C bond length of free BCP (differing from **1a** by 0.123 Å).[23] The two ^{c}Pr rings in **1a** were bent by 36.02° and 37.14° away from the plane of the double bond. The corresponding angles in the cobalt complex were 39.33° and 41.04°, while in bicyclopropyl the rings were at 54.72° to the central C−C bond. There was a decrease in the ^{c}Pr ring angle centered on the double-bond carbon atom from 63.3(1)° to 61.40(14)° and 61.37(15)° upon coordination and a concomitant shortening of the distal ring bond from 1.539(2) Å to 1.516(3) and 1.519(3) Å. This effect was greater in the Co complex, with angles and distal bond lengths of 61.15° and 1.499(12) Å, respectively. The increase of the C═C bond length, the out-of-plane bend of the ^{c}Pr rings, and the shortening of the ring bond and angle were all indicative of the large degree of back-donation and subsequent rehybridization of the double-bond carbon atoms upon coordination.[8,24]

The dppp backbone adopted a chair conformation, with a P−Pt−P angle of 96.762(19)°. A recent search of the Cambridge Crystallographic Database showed that of 81 dppp complexes with one or two platinum atoms, 86% adopted a chair conformation and 9% adopted a boat, while 5% were not sufficiently resolved to determine the conformation. Four of the 81 complexes were Pt(0) species, and of the four, three were trigonal-planar complexes. All four Pt(0) complexes had dppp in a chair conformation.[25−27] These complexes had P−Pt−P angles of 90.99−97.76°, with that of **1a** falling at the top end of the range.

Allylidenecyclopropane: Formation and Coordination Chemistry. It was found that when BCP reacted with [Pt(C_2H_4)$_3$], a ring-opening reaction occurred to form the 1,3-diene, allylidenecyclopropane (ACP) (Scheme 2). This reaction also occurred with [Pt(COD)$_2$], [PtMe$_2$(1,5-hexadiene)], and

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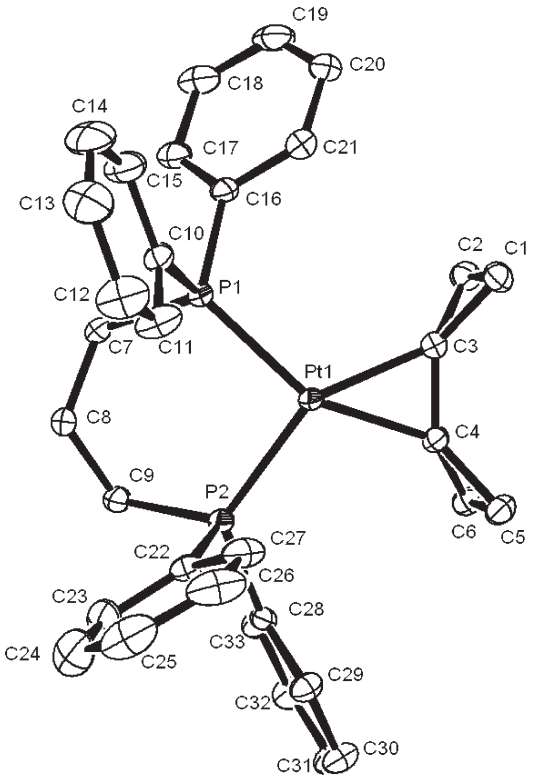
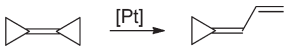


Figure 2. ORTEP diagram of **1a** showing 50% probability thermal ellipsoids. H atoms have been omitted for clarity.

Scheme 2. Synthesis of Allylidenecyclopropane from Bicyclopropylidene

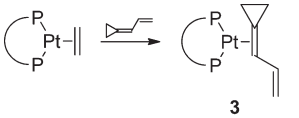


[Pt(norbornene)$_3$]. One previous instance of the formation of ACP from BCP has been reported, occurring in the reaction of BCP with [Pd(OAc)$_2$] and PPh$_3$.[28] The proposed mechanism for this reaction involved the addition of a palladium hydride across the BCP double bond, followed by a cyclopropylmethyl to homoallyl rearrangement and terminated by β-hydride elimination. Under the reported conditions, ACP went on to react with another molecule of BCP to form various oligomers. However, no oligomerization reactions were observed with the above Pt complexes, even after several days at 60 °C.

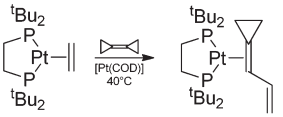
As there were no published reports of any transition metal chemistry with ACP, the formation of Pt-diphosphine complexes containing ACP ligands was investigated. A solution of ACP was produced for these reactions by dissolving a few crystals of [PtMe$_2$(1,5-hexadiene)] in either CDCl$_3$ or C$_6$D$_6$ under inert atmosphere and adding a small amount of BCP. The reaction could then be monitored by NMR for completion, typically reaching ~95% after 5 days. The solution was then used without further purification.

The first transition metal complexes of allylidenecyclopropane (**3a** and **3b**) formed immediately upon addition of the ACP solution to the parent ethene complex [Pt(C$_2$H$_4$)(P−P)] (P−P = dppp, dcyppe) (Scheme 3). ACP could also be generated *in situ* from small amounts of [Pt(COD)$_2$], and the addition

Scheme 3. Synthesis of [Pt(ACP)(P−P)]



Scheme 4. Synthesis of [Pt(ACP)(dbpe)]



of BCP and [Pt(COD)$_2$] to solutions of [Pt(C$_2$H$_4$)(dbpe)], followed by heating at 40 °C, was used to synthesize **3c** (Scheme 4). With 10% [Pt(COD)$_2$] present, the reaction reached 97% completion after heating overnight. The formation of **3c** still occurred when no detectable [Pt(COD)$_2$] was present; however, this reaction only reached 88% completion after 13 days. [Pt(ACP)(dbpx)] could not be synthesized, likely due to the bulk of the phosphine ligand making coordination of the alkene unfavorable.

It was found that when both ACP and BCP were present in the reaction mixture, ACP complexes formed initially. However, the ACP ligand in **3a** was slowly displaced by BCP over several hours at room temperature to generate **1a**. For the dbpe complexes, **3c** was the only product at 40 °C, while at 60 °C, **3c** formed initially before continued heating over several days produced **1c**. It was unclear whether this would also happen for the dcyppe complexes, as **3b** underwent a rearrangement that reached completion too rapidly for displacement to occur (see below). From this we inferred that the complexes of the less bulky ACP were the kinetic products, while the BCP complexes, which had a degree of extra stabilization afforded by alleviation of strain in the second cyclopropyl ring, were the thermodynamic products.

All ACP complexes exhibited second-order ABX ^{31}P NMR spectra similar to the corresponding MCP complexes, with $^1J_{Pt-P}$ couplings for both phosphine environments within 40 Hz of those in **2** (Table 1). The ^{1}H NMR peak of the internal double-bond proton had a large upfield shift from 6.6 ppm in free ACP to 3.4−3.8 ppm in **3** (Table 2). The magnitudes of the $^2J_{Pt-H}$ coupling constants of these protons, 62−68 Hz, were typical of coordination through this bond. The protons of the terminal double-bond have chemical shifts much closer to those in the free alkene. Both the ^{1}H and ^{31}P NMR data indicated that ACP was coordinated via the internal rather than the terminal double-bond, as would be expected given the stabilization afforded by the alleviation of ring strain in the ^{c}Pr ring upon coordination.

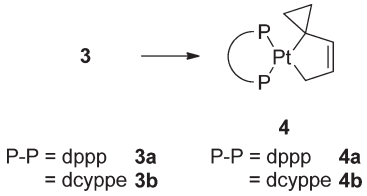
The $^1J_{Pt-C}$ coupling constants of the internal double-bond carbons of **3c** further indicated that the alkene had coordinated via this bond. The coupling constant for the cyclopropyl carbon was 533 Hz, while that of the methyne was 166 Hz, both of which were within 20 Hz of the corresponding value for **2c** (Table 1). The chemical shifts of the carbons of the terminal double-bond were also much closer to those of the free alkene than the internal double-bond carbons (Table 2). In **3c**, the ^{c}Pr double-bond

Table 2. ^{1}H and ^{13}C NMR Data of [Pt(ACP)(P−P)][a]

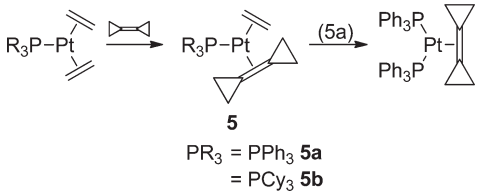
compound		δ_C =CH$_2$	δ_C terminal =CHR	δ_C internal =CHR	δ_C =CR$_2$	δ_C ^{c}Pr	δ_H =CH$_2$	δ_H terminal =CHR	δ_H internal =CHR	δ_H ^{c}Pr
ACP		115.19	120.18	136.88	129.33	2.64	5.18	6.49	6.58	0.93
						2.28	5.05			0.85
[Pt(ACP)(dppp)]	**3a**	[b]	[b]	[b]	[b]	[b]	5.04	6.47	3.78	1.3−0.8
							4.69		$^{2}J_{Pt-H}$ = 67.8 Hz	
[Pt(ACP)(dcyppe)]	**3b**	[b]	[b]	[b]	[b]	[b]	4.85	6.11	3.41	[b]
							4.37		$^{2}J_{Pt-H}$ = 62.1 Hz	
[Pt(ACP)(dbpe)]	**3c**	102.71	147.52	44.72	41.43	10.6	4.98	6.20	3.43	1.5
						9.47	4.64		$^{2}J_{Pt-H}$ = 62.0 Hz	1.0

[a] δ values are given in ppm and J values in Hz. All spectra were measured in C_6D_6 at room temperature. [b] NMR data could not be obtained.

Scheme 5. Rearrangement of [Pt(ACP)(P−P)] to Form Metallocyclopentene Complexes



Scheme 6. Synthesis of [Pt(BCP)(C$_2$H$_4$)(PR$_3$)]



carbons had an AA′X line shape with ^{195}Pt satellites similar to those of the BCP complexes. This was due to the two phosphorus atoms in this complex coincidentally having the same chemical shift.[21] The effect could be seen throughout the carbon spectrum, with all of the resonances of the ACP ligand showing AA′X line shapes. It would be expected that the ACP ligands in **3a** and **3b** would have ABX spectra (with ^{195}Pt satellites) similar to the corresponding MCP complexes, as the phosphorus atoms have different chemical shifts. However, due to the short lifetimes of these complexes, ^{13}C NMR data could not be obtained.

Complexes **3a** and **3b** were unstable in solution, undergoing a rearrangement to form the metallacyclic complexes **4a** and **4b** (Scheme 5). The rearrangement proceeded more rapidly for the dcyppe complex **3b**, with significant amounts of **4b** present within 5 min of addition of the ACP solution and the reaction proceeding to completion after 3 h. For the dppp complex **3a**, the metallacycle appeared in the ^{31}P NMR after 3 h, reaching 96% completion after 7 days.

The formation of metallacyclo-3-pentenes from 1,3-dienes is well established. There are two possible binding modes for these ligands: the η^4:σ^2,π mode, where the double bond is also coordinated to the metal, common for early transition and actinide metals,[29−31] and the planar η^2:σ^2 mode. Planar metallacyclopentene complexes are considered to be intermediates in ring-flipping mechanisms of η^4-diene complexes,[32] and complexes with η^2:σ^2-metallacyclopentene ligands formed from various 1,3-dienes have been reported for Fe,[33,34] Co,[35] Mo,[36] W,[36] Rh,[32,37−39] Ir,[40−43] Pt,[32,44] Ge,[45] and Mg.[46] The NMR data of **4** were consistent with a planar η^2:σ^2-metallacyclopentene structure. The $^{1}J_{Pt-P}$ coupling constants of **4** (1784−1856 Hz) were comparable to those of [Pt(CH$_2$CPh=CHC=CMe$_2$)(dppe)] (1818 and 1842 Hz), which showed that there were Pt−C σ-bonds in **4**.[32] In the previously reported Pt metallacycles, the CH$_2$ groups directly bonded to the metal had δ_H at 2.8−3.2 ppm with $^{2}J_{Pt-H}$ = 68−92 Hz and δ_C at 31−41 ppm with $^{1}J_{Pt-C}$ = 603−787 Hz,[32,44] while the Ir metallacycles had 2.4−3.0 and −2−13 ppm for δ_H and δ_C, respectively.[41] The NMR data of both the Pt−CH$_2$ groups (δ_H = 2.9−3.2 ppm, $^{2}J_{Pt-H}$ = 62−73 Hz, δ_C = 29−39, $^{1}J_{Pt-C}$ = 297−450 Hz) and the Pt−CR$_3$ groups (δ_C = 32−33, $^{1}J_{Pt-C}$ = 959 Hz for **4b**) in **4** agree well with the literature. The NMR data of the double-bond carbons and their attached protons (δ_H = 5.3−6.4 and δ_C = 131−154) also compared favorably to the literature values (δ_H = 5.0−5.6 and δ_C = 135.9−151.3 ppm).[32,41,44]

The rearrangements of **3** to **4** appear to be the first instances of the formation of η^2:σ^2-metallacyclopentene complexes from η^2:π-diene complexes. Previously reported η^2:σ^2-metallacyclopentenes were formed either directly upon addition of the 1,3-diene to a metal precursor[32−34,37−39,44−46] or by rearrangement of an η^4:π-diene complex, generally initiated by the addition of a species such as a Lewis base.[35,36,41,43]

[Pt(L)$_2$(PR$_3$)] Complexes. Precursor complexes containing two ethene ligands and one phosphine ligand were also investigated. Bis-ethene complexes were chosen due to the possibility that oligomerization or isomerization reactions similar to the formation of ACP from BCP might occur. Complexes of the type [M(L)(BCP)(PR$_3$)] (M = Ni, Pd, L = electron-deficient alkene, PR$_3$ = *tert*-butyldiisopropylphosphine, tris(*o*-phenylphenyl)phosphite) have been proposed as intermediates in the palladium- and nickel-catalyzed [3+2] co-cyclization of BCP with various alkenes, but were not isolated.[47] Bis-BCP complexes have also been postulated to be intermediates in the nickel-catalyzed [3+2+2] co-cyclizations.[48]

When BCP was added to [Pt(C$_2$H$_4$)$_2$(PR$_3$)], the product was [Pt(C$_2$H$_4$)(BCP)(PR$_3$)] (**5**) (PR$_3$ = PPh$_3$ (**a**), PCy$_3$ (**b**)) (Scheme 6). For the bulkier PCy$_3$, complex **5b** was stable with an excess of BCP. However, **5a** was stable in solution only when 1

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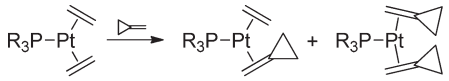
Table 3. Selected NMR Data of $[Pt(L)_2(PR_3)]$[a]

compound		δ_P	$^1J_{Pt-P}$	δ_H ^tPr	J_{Pt-H}	δ_H MCP $=CH_2$	$^2J_{Pt-H}$	δ_H C_2H_4 $=CH_2$	$^2J_{Pt-H}$	δ_C ^tPr	$^1J_{Pt-C}$	δ_C $=CR_2$	$^1J_{Pt-C}$	δ_C $=CH_2$	$^1J_{Pt-C}$
$[Pt(BCP)(C_2H_4)(PPh_3)]$	**5a**	23.17	3094	1.2−0.8	*b*			2.71	51.0	9.2−6.8	*b*	30.16	431.5	54.84	102.2
$[Pt(BCP)(C_2H_4)(PCy_3)]$	**5b**	25.27	2976	1.17−1.05	*b*			2.68	50.0	8.30	23.8	29.08	482.9	50.65	101.8
$[Pt(MCP)(C_2H_4)(PPh_3)]$	**6a**	23.58	3085	1.64	60.0	2.58	61.5	2.61	56.0	*b*	*b*	*b*	*b*	*b*	*b*
				1.55	34.0										
$[Pt(MCP)(C_2H_4)(PCy_3)]$	**6b**	27.97	2978	1.5−0.9	*b*	2.52	61.2	2.49	48.1	*b*	*b*	*b*	*b*	*b*	*b*
$[Pt(MCP)_2(PPh_3)]$	**7a**	22.30	2932	1.31	*b*	2.39	55.0			7.79	24.5	54.05	352.9	38.94	100.3
$[Pt(MCP)_2(PCy_3)]$	**7b**	23.21	2695	1.47−1.29	*b*	2.27	50.0			7.20	25.0	48.45	385.6	32.00	*b*
$[Pt(C_2H_4)_2(PPh_3)]$		24.56	3426					2.82	57.8					42.3	146
$[Pt(C_2H_4)_2(PCy_3)]$		29.20	3296					2.72	56.7					36.9	146

[a] δ values are given in ppm and J values in Hz. All spectra were measured in C_6D_6 at room temperature. [b] NMR data could not be obtained.

Scheme 7. Synthesis of $[Pt(MCP)(C_2H_4)(PR_3)]$ and $[Pt(MCP)_2(PR_3)]$



6 PR_3 = PPh_3 **6a**, PCy_3 **6b** **7** PR_3 = PPh_3 **7a**, PCy_3 **7b**

equiv of BCP was used. When more than 1 equiv was used, $[Pt(BCP)(PPh_3)_2]$ began to form after 40 min and was the only phosphine-containing product after 24 h. The formation of a bis-BCP complex did not occur with either of the phosphines used in this work. This was likely due to the steric constraints of having the two alkenes in a planar coordination geometry as occurs with platinum(0).[49] The double-bond carbons of the BCP ligand had similar chemical shifts (29−30 ppm) and $^1J_{Pt-C}$ (431−483 Hz) to those in **1**, indicating that it was in η^2-coordination (Table 3). The $^1J_{Pt-P}$ coupling constants in both mixed alkene complexes were ∼330 Hz lower than those of the parent bis-ethene complexes, showing the same decrease in $^1J_{Pt-P}$ upon coordination of BCP as was seen for the diphosphine complexes.

Despite the large excesses of MCP used, both the mixed alkene $[Pt(C_2H_4)(MCP)(PR_3)]$ (**6**) and the bis-MCP $[Pt(MCP)_2(PR_3)]$ (**7**) (PR_3 = PPh_3 (**a**), PCy_3 (**b**)) complexes were always formed in a closed system (Scheme 7). The bis-MCP complexes **7** are the first examples of Pt-MCP complexes with more than one MCP ligand. When PPh_3 was used, the product ratio was 80:20 bis-MCP:mixed alkene. The ratio changed to 30:70 in favor of the mixed complex when PCy_3 was used, with the bulkier phosphine hindering but not preventing the coordination of the second MCP ligand. When ethene was allowed to diffuse out of the reaction, complex **7a** was formed in 90% yield. Yields could be improved and complex **7b** formed selectively when inert gas was bubbled through the reaction mixture. The mixed alkene complexes **6** became the major products when ethene was bubbled through the solution. However, the mixed alkene complexes were much less stable than the bis-MCP complexes, as large amounts of ethene regenerated the bis-ethene complexes, while in the presence of free MCP, **7** formed.

The mixed ethene−MCP complexes had $^1J_{Pt-P}$ couplings within 10 Hz of the ethene−BCP complexes **5** (Table 3). ^{13}C NMR data could not be obtained for these complexes due to their instability. However, their ^1H NMR spectra showed similar chemical shifts and $^2J_{Pt-H}$ for the ethene ligands to **5**. The bis-MCP complexes **7** had $^1J_{Pt-P}$ several hundred Hz lower than the parent ethene complex and more than 150 Hz lower than the mixed alkene complex (Table 3). The MCP methylene resonances in the ^1H NMR were also at lower chemical shifts than in the mixed complex and had lower $^2J_{Pt-H}$ (50−55 Hz), closer to those of the ethene rather than the MCP ligand in **6**. Both the carbon and proton NMR data showed that the two MCP ligands were in the same chemical environment on the NMR time scale. While this could be due to rotation of the ligands, it was considered more likely that the ligands were arranged either head-to-head or tail-to-tail. The X-ray crystal structure of **7a** showed that in the solid state the two MCP ligands were tail-to-tail (Figure 3).

The MCP carbon−carbon double-bond length was increased by 5.7% upon coordination, from 1.332(1) Å in free MCP to 1.408(5) Å in **7a**.[50] In $[Rh(MCP)_2(acac)]$, the only other MCP

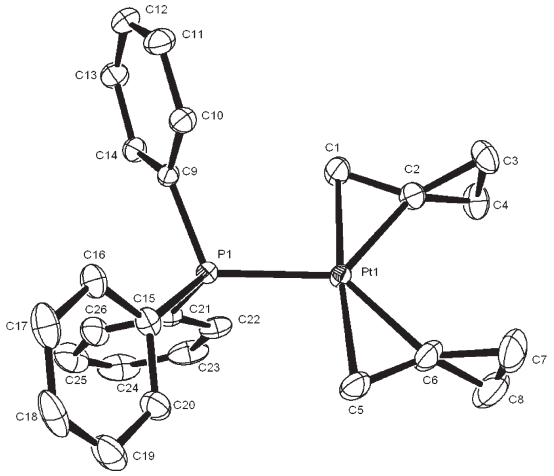


Figure 3. ORTEP diagram of **7a** showing 50% probability thermal ellipsoids. H atoms have been omitted for clarity.

complex characterized by X-ray diffraction, the bond lengths were 1.405(19) and 1.440(19) Å, representing increases of 5.4% and 8.1%, respectively. The increase in MCP bond length upon coordination was much greater than the 1.5% increase in ethene C=C bond length in the related complex $[Pt(C_2H_4)(C_2F_4)(PCy_3)]$.[51,52] The C_2F_4 bond increased by 10.0% upon coordination.[53] The cyclopropyl rings in **7a** were bent by 35.49° and 35.86° away from the plane of the double bond, a greater angle than those in the Rh complex (26.48° and 27.79°). Given the strain of the ^{c}Pr ring, it would be expected that there was a stronger bond from the platinum to the ring double-bond carbon than to the methylene carbon. This was evidenced by the shorter Pt−C distance to the ^{c}Pr carbon (2.087(3) and 2.093(3) Å) than to the methylene (2.130(3) and 2.123(3) Å). The Pt−P bond length was 2.3028(7) Å, shorter than that in $[Pt(C_2H_4)(C_2F_4)(PCy_3)]$, which had a Pt−P distance of 2.343(2) Å.

EXPERIMENTAL SECTION

General Considerations. All reactions were carried out using degassed solvents and standard Schlenk techniques under either a nitrogen or argon atmosphere, unless otherwise stated. Starting materials were purchased from Sigma-Aldrich and used without further purification unless otherwise stated. Bicyclopropylidene,[14] methylenecyclopropane,[13] $[PtCl_2(dppp)]$,[54] $[Pt(C_2H_4)(dbpx)]$,[9] $[Pt(C_2H_4)(dbpe)]$,[9] $[Pt(C_2H_4)_2(PPh_3)]$,[55] and $[Pt(C_2H_4)_2(PCy_3)]$[55] were synthesized according to literature methods. The synthesis of dbpx was via the deprotection of dbpx-borane[56] using neat diethylamine, while dcyppe was synthesized by the reaction of cyclopentylmagnesium bromide with 1,2-bis(dichlorophosphino)ethane. Deuterated solvents were purchased from Sigma-Aldrich and stored under a nitrogen atmosphere. NMR spectra were measured on Varian Unity Inova 300 and 500 MHz and Varian DirectDrive 600 MHz NMR spectrometers, with chemical shift values δ referenced to the residual solvent peaks for ^{1}H and ^{13}C{^{1}H} and to 85% H_3PO_4 for ^{31}P{^{1}H}. Elemental analyses were performed by the Campbell Microanalytical Laboratory, University of Otago, New Zealand. Electrospray ionization mass spectra were performed by the GlycoSyn QC laboratory at Industrial Research Limited using a Waters Q-TOF Premier Tandem mass spectrometer. Calculated NMR spectra were obtained from gNMR spectral simulation program, version 5.0.6.0, written by P. H. M. Budzelaar, IvorySoft 2006. X-ray diffraction data were collected on a Bruker SMART CCD diffractometer using Mo Kα radiation. Data were reduced using Bruker SAINT software. Absorption correction was performed using the SADABS program. The structures were solved using OLEX2 running SHELXS97 and SHELXL97.[57,58] The positions of all hydrogen atoms were calculated during refinement.

Synthesis of [Pt(BCP)(dppp)] (1a). $[Pt(C_2H_4)(dppp)]$ (0.162 g, 0.28 mmol) was dissolved in toluene (3.5 mL). Bicyclopropylidene (0.052 mL, 0.56 mmol) was added, and the solution stirred for 30 min. The solvent was removed *in vacuo*, yielding an off-white solid ([Pt(BCP)(dppp)], 158 mg, 0.23 mmol, 82%). Crystals of [Pt(BCP)(dppp)] were grown by slow recrystallization from hot toluene. ^{1}H NMR (δ, C_6D_6): 7.57(m, 8H, *o*-C_6H_5), 7.04(m, 8H, *m*-C_6H_5), 6.98(m, 4H, *p*-C_6H_5), 2.13(m, 4H, P−CH_2), 1.51(m, 2H, CH_2), 1.29(m, J_{Pt-H} = 66.0 Hz, 4H, ^{c}Pr-*endo*), 1.18(d, 4.4, J_{Pt-H} = 37.3 Hz, 4H, ^{c}Pr-*exo*). ^{13}C NMR (δ, C_6D_6): 136.79(m, *i*-C_6H_5), 132.92(m, *o*-C_6H_5), 129.54(s, *p*-C_6H_5), 128.35(s, *m*-C_6H_5), 34.25(m, J_{P-C} = 73.3, −9.1, J_{P-P} = 24.5, J_{Pt-C} = 409.4 Hz, =CR_2), 28.51(m, P−CH_2), 20.93(m, CH_2), 8.82(s, J_{Pt-C} = 23.1 Hz, ^{c}Pr). ^{31}P NMR (δ, C_6D_6): 9.29(s, $^1J_{Pt-P}$ = 2932 Hz). *m*/*z* = $[M + H]^+$ calcd for $C_{33}H_{35}P_2{}^{194}Pt$ 687.1841; found 687.1849. Anal. Calcd for $C_{33}H_{34}P_2Pt$: C 57.64; H 4.98. Found: C 57.76; H 4.96.

Synthesis of [Pt(MCP)(dppp)] (2a). $[Pt(C_2H_4)(dppp)]$ (87 mg, 0.14 mmol) was dissolved in toluene (1 mL). A large excess of methylenecyclopropane was added, and the solution stirred for 30 min. The solvent was removed *in vacuo*, yielding an off-white solid ([Pt(MCP)(dppp)], 79 mg, 0.13 mmol, 92%). ^{1}H NMR (δ, C_6D_6): 7.77(t, 9 Hz, 4H, *o*-C_6H_5−P_1), 7.51(t, 8.5 Hz, 4H, *o*-C_6H_5−P_2), 7.05(m, 8H, *m*-C_6H_5), 7.00(m, 4H, *p*-C_6H_5), 2.63(dd, J_{P-H} = 7.7, 4.5, J_{Pt-H} = 65.3 Hz, 2H, =CH_2), 2.17(m, 4H, P−CH_2), 1.65(d, 6.5, J_{Pt-H} = 33.0 Hz, 2H, ^{c}Pr-*exo*), 1.59(m, 2H, CH_2), 1.32(d, 9.5, J_{Pt-H} = 82.5 Hz, 2H, ^{c}Pr-*endo*). ^{13}C NMR (δ, C_6D_6): 138.36(m, *i*-C_6H_5−P_1), 136.88(m, *i*-C_6H_5−P_2), 133.17(m, *o*-C_6H_5−P_1), 132.84(m, *o*-C_6H_5−P_2), 129.44(m, *p*-C_6H_5), 128.36(m, *m*-C_6H_5), 42.67(dd, J_{P-C} = 57.3, 5.0, J_{Pt-C} = 455.4 Hz, =CR_2), 28.84(m, P−CH_2), 25.29(dd, J_{P-C} = 36.4, 4.9, J_{Pt-C} = 173.4 Hz, =CH_2), 20.95(m, CH_2), 10.08(d, J_{P-C} = 3.8, J_{Pt-C} = 25.9 Hz, ^{c}Pr). ^{31}P NMR (δ, C_6D_6): 11.76(AB, J_{P-P} = 41.5, $^1J_{Pt-P}$ = 3275 Hz, P_2, *trans* = CH_2), 11.35(AB, J_{P-P} = 41.5, $^1J_{Pt-P}$ = 2975 Hz, P_1, *trans* = CR_2). *m*/*z* = $[M + H]^+$ calcd for $C_{31}H_{33}P_2{}^{194}Pt$ 661.1684; found 661.1678. Anal. Calcd for $C_{31}H_{32}P_2Pt$: C 56.28; H 4.87. Found: C 56.47; H 4.86.

General NMR Synthesis of [Pt(L)(P−P)] (L = BCP (1), MCP (2), P−P = dcyppe (b), dbpx (c), dbpe (d)). $[Pt(C_2H_4)(P-P)]$ (20−50 mg) was dissolved in C_6D_6 (0.5 mL) and placed in an NMR tube. An excess of the alkene was added. For P−P = dbpx, the reactions were heated at 60 °C for up to 6 days, for P−P = dcyppe, the reactions occurred overnight at RT, and for P−P = dbpe the reaction was heated overnight at 40 °C. Yields by NMR ranged from 96% to 100%.

General NMR Synthesis of [Pt(ACP)(P−P)] (3) and [Pt(CH_2CH=CHC$(CH_2)_2$)(P−P)] (4) (P−P = dppp (a), dcyppe (b)). A few crystals of $[PtMe_2(1,5\text{-hexadiene})]$ were placed in an NMR tube, and $CDCl_3$ (0.5 mL) was added. BCP (0.2 mL, 18.7 mmol) was added, and the reaction left for 3 days, after which all of the BCP had reacted to form ACP. $[Pt(C_2H_4)(P-P)]$ (30−100 mg) was placed in an NMR tube, and C_6D_6 (0.5 mL) added. A solution of ACP (0.1 mL, 27 M solution in $CDCl_3$) was added, resulting in the immediate formation of [Pt(ACP)(P−P)]. After several hours, the complex rearranges to form [Pt(CH_2CH=CHC$(CH_2)_2$)(P−P)] (91−93%).

Synthesis of [Pt(ACP)(dbpe)] (3c). $[Pt(C_2H_4)(dbpe)]$ (100 mg, 0.185 mmol) was dissolved in C_6D_6 (0.5 mL) and placed in an NMR tube. BCP (0.02 mL, 1.87 mmol) was added, and the solution heated at 40 °C for 13 days. [Pt(ACP)(dbpe)] fromed, 88% by NMR. X-ray quality crystals were grown by slow recrystallization from hot toluene. ^{1}H NMR (δ, C_6D_6): 6.20(dt, 16.2, 9.6 Hz, 1H, =CHR), 4.98(m,

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1H, =CH_2), 4.64(m, 1H, =CH_2), 3.43(m, J_{Pt-H} = 62.0 Hz, 1H, =CHR), 1.9−1.5(m, 6H, P−CH_2 and ^{c}Pr), 1.16(d, 12.5 Hz, 9H, ^{t}Bu), 1.15(d, 12.5 Hz, 9H, ^{t}Bu), 1.03(d, 12.0 Hz, 9H, ^{t}Bu), 1.02(d, 12.5 Hz, 9H, ^{t}Bu), 1.0(m, 2H, ^{c}Pr). ^{13}C NMR (δ, C_6D_6): 147.52(t, J_{P-C} = 4.6, J_{P-P} = −34.3, J_{Pt-C} = 56.4 Hz, =CHR), 102.71(t, J_{P-C} = 8.6, J_{P-P} = −25.3, J_{Pt-C} = 42.9 Hz, =CH_2), 44.72(dd, J_{P-C} = 38.1, 2.0, J_{P-P} = −57.7, J_{Pt-C} = 165.5 Hz, =CHR), 41.43(m, J_{P-C} = 70.3, 2.3, J_{P-P} = 65.8, J_{Pt-C} = 533.1 Hz, =CR_2), 36.51(dd, J_{P-C} = 12.8, 4.6, J_{P-P} = −27.1, J_{Pt-C} = 46.8 Hz, P−CR_3), 35.75(dd, J_{P-C} = 11.5, 5.1, J_{P-P} = −24.3, J_{Pt-C} = 44.0 Hz, P−CR_3), 35.50(dd, J_{P-C} = 13.2, 3.4, J_{P-P} = −31.2, J_{Pt-C} = 53.8 Hz, P−CR_3), 34.81(dd, J_{P-C} = 14.5, 5.4, J_{P-P} = −31.2, J_{Pt-C} = 60.0 Hz, P−CR_3), 30.5−29.5(m, CH_3), 26.43(t, 35.8, J_{Pt-C} = 12.7 Hz, P−CH_2), 25.22(t, 18.0, J_{Pt-C} = 10.4 Hz, P−CH_2), 10.60(t, J_{P-C} = 3.3, J_{P-P} = −10.4, J_{Pt-C} = 17.7 Hz, ^{c}Pr), 9.47(t, J_{P-C} = 2.0, J_{P-P} = −8.9, J_{Pt-C} = 15.5 Hz, ^{c}Pr). ^{31}P NMR (δ, C_6D_6): 96.40(AB, J_{P-P} = 62.2, $^1J_{Pt-P}$ = 2848 Hz), 96.39(AB, J_{P-P} = 62.2, $^1J_{Pt-P}$ = 3196 Hz). m/z = $[M + H]^+$ calcd for $C_{24}H_{49}P_2{}^{194}Pt$ 593.2936; found 593.2946 $[M + H^+]$.

Synthesis of [Pt(BCP)(C_2H_4)(PPh$_3$)] (5a). [Pt(C_2H_4)$_2$(PPh$_3$)] (20 mg, 0.039 mmol) was dissolved in hexane (2 mL) under an ethene atmosphere. BCP (3.6 μL, 0.34 mmol) was added, and the reaction stirred for 5 min. The solution was cooled to −78 °C for an hour, after which the supernatant was decanted off, leaving a white solid ([Pt(BCP)(C_2H_4)(PPh$_3$)], 15 mg, 0.027 mmol, 70%). ^{1}H NMR (δ, C_6D_6): 7.52(m, 6H, o-C_6H_5), 7.00(m, 9H, m- and p-C_6H_5), 2.71(s, J_{Pt-H} = 51.0 Hz, 4H, =CH_2), 1.2−0.8(brs, 8H, ^{c}Pr). ^{13}C NMR (δ, C_6D_6): 134.61(d, 43.1, J_{Pt-C} = 25.5 Hz, i-C_6H_5), 134.22(d, 12.4, J_{Pt-C} = 18.2 Hz, o-C_6H_5), 129.88(d, 2.4 Hz, m-C_6H_5), 128.36(s, p-C_6H_5), 54.84(d, 2.9, J_{Pt-C} = 102.2 Hz, =CH_2), 30.16(d, 16.3, J_{Pt-C} = 431.5 Hz, =CR_2), 9.2−6.8(brs, ^{c}Pr). ^{31}P NMR (δ, C_6D_6): 23.17(s, $^1J_{Pt-P}$ = 3094 Hz).

Synthesis of [Pt(BCP)(C_2H_4)(PCy$_3$)] (5b). [Pt(C_2H_4)$_2$(PCy$_3$)] (63 mg, 0.12 mmol) was dissolved in hexane (3 mL) under an ethene atmosphere. An excess of BCP (0.02 mL, 1.9 mmol) was added, and the solution stirred for 30 min. The solution was reduced to approximately 0.5 mL and cooled to −78 °C. After an hour, the supernatant was decanted, leaving a pale yellow solid ([Pt(BCP)(C_2H_4)(PCy$_3$)], 53 mg, 0.091 mmol, 76%). ^{1}H NMR (δ, C_6D_6): 2.68(s, J_{Pt-H} = 50.0 Hz, 4H, =CH_2), 2.03(d, 10.0, J_{Pt-H} = 23.0 Hz, 3H, P−CH) 1.86(d, 12.5 Hz, 6H, CH_2), 1.64(d, 11.0 Hz, 6H, CH_2), 1.54(d, 12.5 Hz, 3H, CH_2), 1.35(qm, 13.0 Hz, 6H, CH_2), 1.17−1.05(m, 11H, ^{c}Pr and CH_2), 1.02(quintt, 13.0, 3.0 Hz, 6H, CH_2). ^{13}C NMR (δ, C_6D_6): 50.65(d, 1.9, J_{Pt-C} = 101.8 Hz, =CH_2), 36.46(d, 20.6, J_{Pt-C} = 26.0 Hz, P−CH), 30.27(s, J_{Pt-C} = 17.8 Hz, CH_2), 29.08(s, J_{Pt-C} = 482.9 Hz, =CR_2), 27.93(d, 10.1 Hz, CH_2), 26.82(s, CH_2), 8.30(brs, J_{Pt-C} = 23.8 Hz, ^{c}Pr). ^{31}P NMR (δ, C_6D_6): 25.27(s, $^1J_{Pt-P}$ = 2976 Hz).

Synthesis of [Pt(MCP)(C_2H_4)(PPh$_3$)] (6a). [Pt(C_2H_4)$_2$(PPh$_3$)] (10 mg, 0.019 mmol) was dissolved in hexane (1.5 mL) under an ethene atmosphere. An excess of MCP was added, and the solution flushed with C_2H_4 for 5 min. The volume was reduced to ∼0.5 mL, and the solution cooled to −78 °C for an hour. The supernatant was decanted off, leaving pale white crystals. [Pt(MCP)(C_2H_4)(PPh$_3$)] formed, 47% by NMR. ^{1}H NMR (δ, C_6D_6): 7.52(m, 6H, o-C_6H_5), 7.01(m, 9H, m- and p-C_6H_5), 2.61(s, J_{Pt-H} = 56.0 Hz, 4H, C_2H_4 =CH_2), 2.58(d, 6.5, J_{Pt-H} = 61.5 Hz, 2H, MCP =CH_2) 1.64(brd, 7.5, J_{Pt-H} = 60.0 Hz, 2H, ^{c}Pr), 1.55(d, 5.5, J_{Pt-H} = 34.0 Hz, 2H, ^{c}Pr). ^{31}P NMR (δ, C_6D_6): 23.58(s, $^1J_{Pt-P}$ = 3085 Hz).

Synthesis of [Pt(MCP)(C_2H_4)(PCy$_3$)] (6b). [Pt(C_2H_4)$_2$(PCy$_3$)] (12 mg, 0.023 mmol) was placed in an NMR tube under an ethene atmosphere, and C_6D_6 (0.5 mL) added. An excess of MCP was added, and the solution flushed with C_2H_4 for 5 min. [Pt(MCP)(C_2H_4)(PCy$_3$)] formed, 94% by NMR. In the presence of excess MCP, [Pt(MCP)$_2$(PCy$_3$)] forms overnight. ^{1}H NMR (δ, C_6D_6): 2.52(d, 6.3, J_{Pt-H} = 61.2 Hz, 2H, MCP =CH_2), 2.49(s, J_{Pt-H} = 48.1 Hz, 4H, C_2H_4 =CH_2), 2.20(m, 3H, P−CH), 1.90(d, 12.0 Hz, 6H, CH_2), 1.7−1.5(m, 9H, CH_2), 1.5−0.9(m, 19H, ^{c}Pr and CH_2). ^{31}P NMR (δ, C_6D_6): 27.97(s, $^1J_{Pt-P}$ = 2978 Hz).

Synthesis of [Pt(MCP)$_2$(PPh$_3$)] (7a). [Pt(C_2H_4)$_2$(PPh$_3$)] (70 mg, 0.14 mmol) was suspended in hexane (5 mL). An excess of MCP was added, and the reaction stirred for 15 min. Hexane was added to dissolve the remaining solid. The solution was cooled to −78 °C for an hour, after which the supernatant was decanted off, leaving an off-white solid. Solid was 90% [Pt(MCP)$_2$(PPh$_3$)], 10% [Pt(MCP)(C_2H_4)(PPh$_3$)]. X-ray quality crystals of [Pt(MCP)$_2$(PPh$_3$)] were grown by recrystallization from hexane containing a few drops of MCP. ^{1}H NMR (δ, C_6D_6): 7.52(m, 6H, o-C_6H_5), 7.00(m, 9H, m- and p-C_6H_5), 2.39(d, 4.0, J_{Pt-H} = 55.0 Hz, 4H, =CH_2), 1.31(m, 4H, ^{c}Pr). ^{13}C NMR (δ, C_6D_6): 138.81(d, 39.1, J_{Pt-C} = 26.9 Hz, i-C_6H_5), 134.22(m, o-C_6H_5), 129.83(d, 2.4 Hz, m-C_6H_5), 128.35(s, p-C_6H_5), 54.05(d, 16.3, J_{Pt-C} = 352.9 Hz, =CR_2), 38.94(s, J_{Pt-C} = 100.3 Hz, =CH_2), 7.79(s, J_{Pt-C} = 24.5 Hz, ^{c}Pr). ^{31}P NMR (δ, C_6D_6): 22.30(s, $^1J_{Pt-P}$ = 2932 Hz).

Synthesis of [Pt(MCP)$_2$(PCy$_3$)] (7b). [Pt(C_2H_4)$_2$(PCy$_3$)] (12 mg, 0.023 mmol) was placed in an NMR tube under an ethene atmosphere, and C_6D_6 (0.5 mL) added. A large excess of MCP was added, and Ar bubbled through the solution for 5 min. [Pt(MCP)$_2$(PCy$_3$)] formed, 99% by NMR. ^{1}H NMR (δ, C_6D_6): 2.27(d, 6.0 J_{Pt-H} = 50.0 Hz, 4H, =CH_2), 2.21(d, 8.5, J_{Pt-H} = 24.0 Hz, 3H, P−CH), 1.88(d, 12.0 Hz, 6H, CH_2), 1.65(dd, 13.0, 2.0 Hz, 6H, CH_2), 1.55(d, 12.0 Hz, 3H, CH_2), 1.47−1.29(m, 11H, ^{c}Pr and CH_2), 1.13(m, 6H, CH_2), 1.03(m, 6H, CH_2). ^{13}C NMR (δ, C_6D_6): 48.45(brd, 28.3, J_{Pt-C} = 385.6 Hz, =CR_2), 36.72(d, 21.1, J_{Pt-C} = 26.9 Hz, P−CH), 32.0(m, =CH_2), 30.34(s, J_{Pt-C} = 18.2 Hz, CH_2), 28.02(d, 10.2 Hz, CH_2), 26.90(s, CH_2), 7.20(s, J_{Pt-C} = 25.0 Hz, ^{c}Pr). ^{31}P NMR (δ, C_6D_6): 23.21(s, $^1J_{Pt-P}$ = 2695 Hz).

CONCLUSION

A range of η^2-complexes of bicyclopropylidene and methylenecyclopropane of the formula [Pt(L)(P−P)] were synthesized with various diphosphine ligands. Mixed alkene complexes of BCP and MCP of the type [Pt(C_2H_4)(L)(PR$_3$)] were synthesized from the bis-ethene precursor. These complexes are similar to the proposed intermediates in the palladium- and nickel-catalyzed [3 +2] co-cyclization of BCP with various alkenes.[47] While bis-MCP complexes could be synthesized, bis-BCP complexes were not formed, most likely due to steric constraints. These complexes are the first examples of late transition metal complexes of bicyclopropylidene as well as the first bis-methylenecyclopropane complexes of platinum.

It was found that when BCP was reacted with a number of Pt(0) and Pt(II) complexes, a ring-opening reaction occurred to form allylidenecyclopropane. The coordination chemistry of ACP was also explored, with the synthesis of the diphosphine complexes [Pt(ACP)(P−P)]. Some of the ACP complexes underwent a rearrangement reaction to form η^2:σ^2-metallacyclopentene complexes, the first examples of the first instances of the formation of η^2:σ^2-metallacyclopentene complexes from η^2:π-diene complexes, rather than from η^4:π-diene complexes. This work is the first exploration of the transition metal chemistry of allylidenecyclopropane.

ASSOCIATED CONTENT

Supporting Information. Text giving experimental methods and characterization data for **1b**−**d**, **2b**−**d**, **3a**,**b**, **4**, [Pt(C_2H_4)-(dppp)], [$PtCl_2$(dcyppe)], and [Pt(C_2H_4)(dcyppe)]. X-ray crystallographic files in CIF format for [Pt(BCP)(dppp)] (**1a**) and [Pt(MCP)$_2$(PPh$_3$)] (**7a**). This material is available free of charge via the Internet at http://pubs.acs.org.

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