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Addition reactions of mononuclear η^3-allenyl/propargyl transition metal complexes: a new class of potent organometallic carbon electrophiles

Jwu-Ting Chen *

Department of Chemistry, National Taiwan University, Taipei 106, Taiwan, ROC

Contents

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* Tel.: +886-2-2366-0352; fax: +886-2-2363-6359.
E-mail address: jtchen@ccms.ntu.edu.tw (J.-T. Chen)

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Abstract

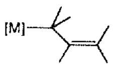
The cationic mononuclear η^3-allenyl/propargyl complexes exhibit new non-classical organometallic bonding of σ,π-mode and remarkable activity of potent carbon electrophiles. The organic moieties of the title species, general formula R′R″CCCR, use all three adjacent unsaturated carbons to bond with metal in a unique coplanar manner. The C_3 skeletons thus are severely distorted from the normal linear configuration to $150 \pm 5°$. The R′R″C–C distances are in the range of long double bonds; whereas C–CR are between double and triple bonds, indicating the resonance structures of allenyl and propargyl. The cationic complexes with η^3-allenyl/propargyl ligands can undergo feasible reactions of regioselective nucleophilic addition which provide a pragmatic synthetic access to new organometallic species of central-carbon-substituted η^3-allyl, η^3-oxa- and η^3-aza-trimethylenemethane. The broad spectrum of C–Nu bond formation encompasses hydroxylation, alkoxylation, phenoxylation, acyloxylation, thioxylation, thio- and seleno-phenoxylation, amination, amidation, phosphination, etc. As to carbation, the η^3-allenyl/propargyl complexes react with carbanions to form η^3-trimethylenemethane complexes. The electrophilicity of η^3-C_3H_3 allows us to conduct regioselective carbon–carbon coupling with the electron-rich aromatics to achieve aromatic electrophilic substitution. Although both η^3-allenyl/propargyl and η^1-allenyl complexes are essentially subject to similar nucleophilic addition, the former are distinctly more reactive and versatile. From the mechanistic viewpoint, the cationic η^3-allenyl/propargyl complexes prefer to undergo external nucleophilic attack at the central carbon. In contrast, nucleophilic addition to the η^1-allenyl complexes requires preceding coordination of the nucleophile to a metal.

Keywords: η^3-Allenyl/propargyl complexes; Nucleophilic addition; Aromatic electrophilic substitution

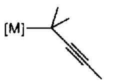
1. Introduction

Transition metal complexes with unsaturated hydrocarbons which are π-bonded to the metal have long been the focus of organometallic chemistry. Those with non-classical organometallic interactions are of particular interest, for they often empower new activity to the organic moieties [1]. For example, organic allyls (C_3R_5–) often bond with metal in a η^3-form rather than a conventional η^1-form in organic chemistry. The chemistry involving η^3-allyl complexes has been extensively studied and proven to contribute immensely to organic synthesis [2].

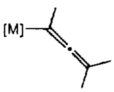
Propargyl which may be conceived as the alkyne analog of allyl has a tautomeric isomer of allenyl. Both propargyl and allenyl (C_3R_3–) groups have three-carbon skeletons and unsaturated hydrocarbyl functionalities. Such structural features are similar to the allyl group and are expected to have a rich chemistry with a metal. Indeed, transition metal complexes of allenyl and propargyl have drawn attention for 3 decades, since the first reported synthesis of metal η^1-allenyl [3].



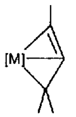
η^1-allyl



η^1-propargyl



η^1-allenyl



σ,π-allenyl/propargyl

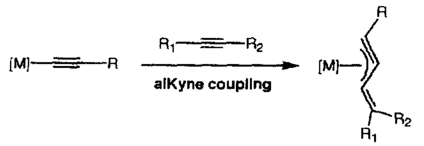
Organometallic propargyl and allenyl complexes have revealed their synthetic utility in many organic reactions [3,4]. However, mononuclear allenyl or propargyl metal complexes with non-classical σ,π-bonding were actually unexplored until recently.

Metal η^1-propargyl can transform into the thermodynamically more stable η^1-allenyl tautomer [5]. The mechanistic studies of this process of tautomerization indicate the involvement of a 1,3-metal shift. Comparing such a metal shift with the η^1-to-η^3-to-η^1 motion of allyl [6], it would be chemically logical to expect the η^3-bonding interaction between the metal and the allenyl or propargyl ligands. Recent development in metal η^3-allenyl/propargyl chemistry has filled such a category and opened a new page in organometallic chemistry. We choose to use the nomenclature of η^3-allenyl/propargyl, because the organic ligands with a general C_3R_3 formula are shown to bond with metal through all three carbon atoms and possess the resonance structures between allenyl and propargyl. Such a bonding mode of η^3-C_3R_3 groups remarkably enhances their electrophilic character, especially at the central carbon, and makes them behave as potent organometallic carbon electrophiles [7]. In fact, the cationic mononuclear η^3-allenyl/propargyl complexes are prone to external attack by a variety of hard and soft nucleophiles. A couple of previous reviews have covered the synthesis and some results of early investigation for these title complexes [3g,8]. This article is prompted by the rapid development of their reactivity. We will concentrate more on the reaction scope of nucleophilic addition and trace the literature up to 1998.

2. Mononuclear η^3-allenyl/propargyl transition metal complexes

2.1. Synthesis

Different synthetic routes have been developed to prepare the mononuclear η^3-allenyl/propargyl complexes. The transition metals involved, include Os, Ru, Fe, W, Mo, Re, Zr, Ti, Pt, and Pd. In 1985, Werner et al. discovered an osmium complex $[Os(PMe_3)_4(\eta^3\text{-}PhCCC{=}CHPh)](PF_6)$, resulting from oxidative coupling of two alkynyl groups [9a]. The first dozen examples of the isolable η^3-allenyl/propargyl complexes all contain a η^3-butenynyl moiety (RCCC=CR′R″) which is generally formed by incorporating two 'ynes' [9]. The typical reactions comprise the alkyne coupling (Eq. 1), alkyne-vinylidene coupling (Eq. 2), as well as enynyl rearrangement (Eq. 3), etc.



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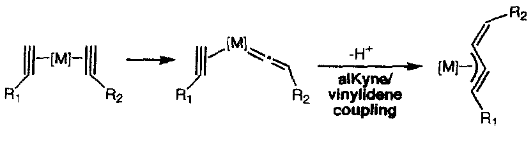

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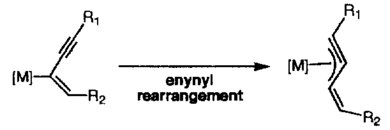

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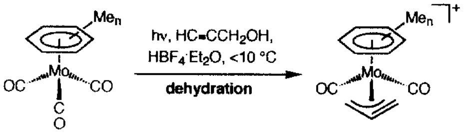
The first unsubstituted η^3-allenyl/propargyl complexes $[(Me_nC_6H_{6-n})Mo(CO)_2(\eta^3\text{-}HCCCH_2)]^+$ (**1**) were reported by Krivykh and his coworkers in 1991 [10a]. A one-pot reaction containing propargyl alcohol, $HBF_4{\cdot}Et_2O$, and the coordination-unsaturated molybdenum complex derived from $(Me_nC_6H_{6-n})\text{–}Mo(CO)_3$ under UV irradiation provided a compound with a η^3-$HCCCH_2$ ligand (Eq. 4). Similar reactions with tungsten and rhenium complexes also yield the corresponding cationic η^3-allenyl/propargyl products $[(Mesityl)\text{-}W(CO)_2(\eta^3\text{-}HCCCH_2)]^+$ and $[Cp^*Re(CO)_2(\eta^3\text{-}HCCCH_2)]^+$ [10b]. The related complexes of the latter rhenium cation, $[Cp^*Re(CO)_2(\eta^3\text{-}RCCCHR')]^+$ (R = H R′ = Me **2a**, Et **2b**, ^{t}Bu **2d**; R = Me R′ = Me **2e**, Et **2f**), were acquired by Casey and his coworkers mainly via an alternative route from the coordinated alkynes in the formula of $RC{\equiv}CCH_2R'$ by hydride abstraction (Eq. 5) [11].



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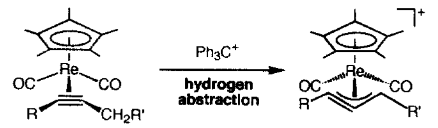

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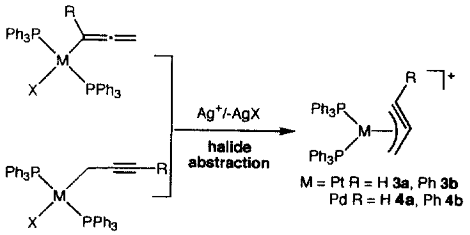
(5)

Meanwhile, our laboratory succeeded in preparing the cationic platinum and palladium complexes containing unsubstituted η^3-allenyl/propargyl ligand, $[M(PPh_3)_2(\eta^3\text{-}HCCCH_2)]^+$ (M = Pt **3a**, Pd **4a**) (Eq. 6) [12]. The synthetic strategy was to open a coordination site from the η^1-allenyl(halo) complexes *trans*-$M(PPh_3)_2(X)(\eta^1\text{-}CHCCH_2)$ (X = Cl, Br) by halide abstraction. Wojcicki and Kurosawa also reported the substituted derivatives $[M(PPh_3)_2(\eta^3\text{-}RCCCH_2)]^+$ (M = Pt. R = Ph **3b**, Me **3c**; M = Pd. R = Ph **4b**) using the same synthetic methodology from either η^1-allenyl or η^1-propargyl species (Eq. 6) [13]. Kurosawa could extend this method to achieve the synthesis of neutral η^3-allenyl/propargyl palladium complexes $Pd(X)(PPh_3)(\eta^3\text{-}RCCCH_2)$ (R ≠ H **5**) by eliminating a phosphine ligand (Eq. 7) [14].



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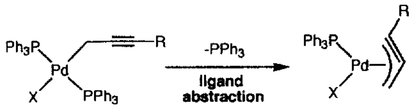

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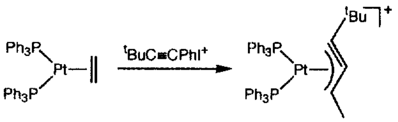
Stang and his coworkers synthesized other substituted η^3-allenyl/propargyl platinum complexes by adding alkynyl(phenyl) iodonium salts to a d^{10} ethylene complex $Pt(PPh_3)_2(C_2H_4)$ (Eq. 8) [15]. Other synthetic methods such as reactions of propargyl ether with Lewis acids (Eqs. 9, 10) [9n,13a], transmetallation by propargyl Grignard nucleophiles (Eq. 11) [16], and reactions of propargyl halide with organotitanium (Eq. 12) [17] can accomplish the preparation for various title species as well.



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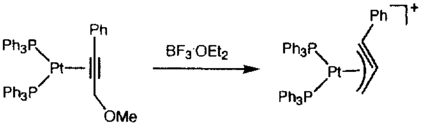

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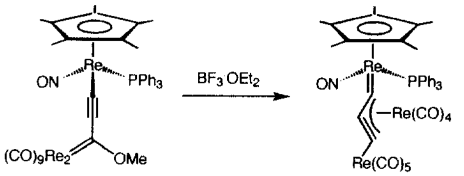

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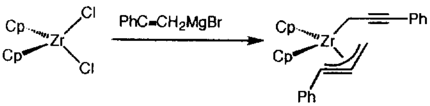

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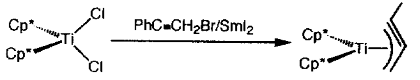

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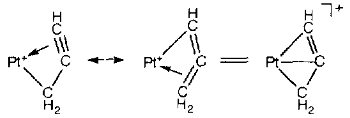
2.2. NMR and structural characteristics

Although there have been η^3-allenyl/propargyl species proposed on the basis of NMR evidence [18], vigorous NMR spectroscopic characterization for such complexes is not quite straightforward. This is because these complexes not only have severely distorted non-classical configuration, but often also contain substituents and more than one quaternary carbon. Detailed comparison of the NMR spectroscopic data has been done in the previous reviews [8a]. A few new species are added and shown in Table 1.

The complexes containing η^3-HCCCH$_2$ are of the prototype, which provide particularly useful diagnostic NMR data [10a,12,19]. In the ^{31}P-NMR spectra of $[M(PPh_3)_2(\eta^3\text{-HCCCH}_2)](BF_4)$ (M = Pt **3a** and Pd **4a**), two different phosphine signals afford evidence for unsymmetric η^3-HCCCH$_2$. Comparably, $[(C_6H_3Me_3)Mo(CO)_2(\eta^3\text{-HCCCH}_2)]^+$ (**1**) has distinct ^{13}C-NMR data for two carbonyls. The ^{1}H-NMR spectra of **3a** shows two resonances with an integration ratio of 2:1 at δ 2.91 and 4.60. Similar to the η^1-allenyl complexes, the CH resonance of **3a** is more downfield than that of CH$_2$. But, the comparable values of $J_{\text{H-Pt}}$ for $C\underline{H}$ (27.2 Hz) and for $C\underline{H}_2$ (30.8 Hz) indicate that both carbon termina are attached to the metal. The small values of $^4J_{\text{HH}}$ (2.2–2.4 Hz) are similar to those of η^1-CH$_2$C≡CH [5] but smaller than those of η^1-CH=C=CH$_2$ (6.4 Hz) [8a,19]. The magnetic equivalency of the CH$_2$ in complexes **3**, **4**, and **5** is consistent with their coplanar coordination sphere of P$_2$MC$_3$. In contrast, the two methylene hydrogens in complexes **1** and **2** are non-equivalent since they lack the symmetric molecular plane. The geminal coupling constants for CH$_2$ are relatively large (ca. 10 Hz) in complexes with a piano-stool geometry.

The ^{1}H-coupled ^{13}C-NMR data are most revealing. In the spectrum of **3a**, a resonance at δ 101.6 with $^2J_{\text{C-H}}$ of 29 Hz is assigned to the quaternary central carbon. It is clearly distinguishable from the β-carbon of η^1-allenyl. A doublet at δ 90.8 with a large $^1J_{\text{C-H}}$ value (246 Hz) is attributed to the propargyl terminus CH as in form **A**. A triplet at δ 51.8 with $^1J_{\text{C-H}} = 171$ Hz, which is too large to be explained by common sp^3 carbon but is close to the C$_t$ of η^3-allyl, fits an η^3-allenyl resonance of structure **B**.



A **B**

The π-attachment of the C$_3$R$_3$ moiety is also supported by the coupling constants $J_{\text{C-Pt}}$: 54–63 for C$_c$, 93–114 for CH$_2$, and 126–137 Hz for CH. Such a highly strained C3 framework is indicated by the large $J_{\text{P-Pt}}$ values (3743–3810 and 4179–4285 Hz) which are comparable to those in the η^2-alkene and η^2-alkyne complexes [2b]. The chemical shift of the η^3-allenyl/propargyl central carbon, which apparently varies with metal, is another sign for a M–C$_c$ bonding interaction.

X-ray crystallography affords the technique for authentic identification of the mononuclear η^3-allenyl/propargyl complexes [10a,13b,14a,15]. The most characteristic feature of the η^3-C$_3$R$_3$ ligands is their coplanar unsymmetrical propensity. In comparison with other known tricarbon organometals, the η^3-allyl [20] and metallacyclobutane [21] complexes have folded structures. The metallacyclobutene [22] and deprotiometallacyclobutadiene complexes [23] are planar, nevertheless, with no bonding between the metal and the central carbon.

Table 1
Characteristic ^{13}C-NMR and structural data of η^3-allenyl/propargyl complexes

Compound	Cc ^{b} (δ)	M–C$_t$ ^{c} M–C$'_t$ (Å)	M–C$_c$ ^{c} (Å)	C$_c$–C$_t$ ^{c} C$_c$–C$'_t$ (Å)	$\angle$C$_t$C$_c$C$'_t$ ^{c} (°)	Ref.
[Os(PMe$_3$)$_4$(η^3-PhCCC=CHPh)]$^+$	–	2.15	2.21	1.39	150	[9a]
		2.39		1.29		
[Ru(Cyttp)(C≡CPh)$_2$ ^{a}	–	2.200	2.191	1.379	148.7	[9b]
(η^3-PhCCC=CHPh)]$^+$		2.258		1.249		
[RuCl(Cyttp)(η^3-PhCCC=CHPh)]$^{+\ a}$	–	2.040	2.229	1.416	154.3	[9f]
(synmer)		2.558		1.220		
[RuCl(Cyttp)(η^3-PhCCC=CHPh)]$^{+\ a}$	–	2.084	2.169	1.396	148.2	[9f]
(antimer)		2.319		1.248		
[Ru(Cyttp)(C≡CPh)	–	2.200	2.191	1.379	148.7	[9f]
(η^3-PhCCC=CHPh)]$^+$ (mer) ^{a}		2.258		1.249		
[(C$_5$Me$_5$)W(CO)$_2$–	45.8	2.244	2.296	1.369	145.0	[9f]
(η^3-^{t}BuCCC=CMe^{t}Bu)]$^+$		2.328		1.27		
[Ru(PP$_3$)	–	2.144	2.234	1.392	154.0	[9h]
(η^3-TMSCCC=CHCH$_2$TMS)]$^+$		2.485		1.247		
[Ru(PP$_3$)(η^3-PhCCC=CHPh)]$^+$	57.8	–	–	–	–	[9i]
[Ru(PPh(OEt)$_2$)$_4$	ca. 115	2.135	2.244	1.39	150.9	[9j]
(η^3-TolCCC=CHTol)]$^+$		2.430		1.23		
[Ru(Cl)(PPh$_3$)$_2$(CO)–	110.0	2.282	2.192	1.398	157.1	[9k]
(η^3-TMSCCC=CHCH$_2$TMS)]$^+$		2.366		1.250		
[Ru(PPh$_3$)$_2$(CO)$_2$-	–	2.170	2.233	1.371	147.4	[9n]
(η^3-PhCCC=CHPh)]$^+$		2.320		1.244		
[Fe(dmpe)$_2$(η^3-PhCCC=CHPh)]$^+$	51	1.987	2.094	1.398	149.0	[9m]
		2.305		1.243		
[Fe(depe)$_2$(η^3-MeCCC=CHMe)]$^+$	–	2.048	2.113	1.321	144.8	[9m]
		2.196		1.296		
[(C$_6$Me$_5$H)Mo(CO)$_2$(η^3-HCCCH$_2$)]$^+$	69.9	2.319	2.282	1.380	150.9	[10a]
		2.340		1.236		

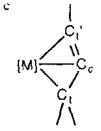
Table 1 (Continued)

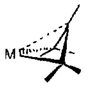
Compound	Cc [b] (δ)	M–C$_t$ [c] M–C$'_t$ (Å)	M–C$_c$ [c] (Å)	C$_c$–C$_t$ [c] C$_c$–C$'_t$ (Å)	∠C$_t$C$_c$C$'_t$ [c] (°)	Ref.
$[(C_5Me_5)Re(CO)_2(\eta^3\text{-}MeCCCH_2)]^+$	56.7	–	–	–	–	[11b]
$[(C_5Me_5)Re(CO)_2(\eta^3\text{-}EtCCCH_2)]^+$	57.8	–	–	–	–	[11b]
$[(C_5Me_5)Re(CO)_2(\eta^3\text{-}MeCCCHMe)]^+$	59.8	–	–	–	–	[11b]
$[(C_5Me_5)Re(CO)_2(\eta^3\text{-}EtCCCHMe)]^+$	60.8	–	–	–	–	[11b]
$[(C_5Me_5)Re(CO)_2(\eta^3\text{-}{}^tBuCCCH_2)]^+$	60.5	2.305	2.239	1.38	153	[11b]
		2.345		1.26		
$[Pd(PPh_3)_2(\eta^3\text{-}HCCCH_2)]^+$	100.6	–	–	–	–	Unpublished
$[Pt(PPh_3)_2(\eta^3\text{-}HCCCH_2)]^+$	101.6	–	–	–	–	[12]
$[Pd(PPh_3)_2(\eta^3\text{-}MeCCCH_2)]^+$	91.2	–	–	–	–	[13b]
$[Pd(PPh_3)_2(\eta^3\text{-}PhCCCH_2)]^+$	94.6	2.162	2.143	1.38	154	[13c]
		2.334		1.22		
$[Pt(PPh_3)_2(\eta^3\text{-}PhCCCH_2)]^+$	97.3	2.186	2.150	1.39	152	[13a]
		2.273		1.23		
$Pd(C_6F_5)(PPh_3)(\eta^3\text{-}{}^tBuCCCH_2)$	–	2.156	2.116	1.38	151.6	[14a]
		2.238		1.244		
$[Pt(PPh_3)_2(\eta^3\text{-}{}^tBuCCCHMe)]^+$	94.2	2.243	2.140	1.390	154.1	[15]
		2.265		1.266		
$[Pd(PPh_3)_2(\eta^3\text{-}Me_3SiCCCH_2)]^+$	113.8	–	–	–	–	[13c]
$(C_5H_5)_2Zr(Me)(\eta^3\text{-}PhCCCH_2)$	98.8	2.361	2.438	1.344	155.4	[16]
		2.658		1.259		
$[(CO)_4Re[\eta^3\text{-}(CO)_5ReCCC{=}Re(C_5Me_5)(NO)(PPh_3)]^+$	297.1	2.24	2.27	1.41	152	[9n]
		2.43		1.28		

[a] Cyttp = $PhP[CH_2)_3P(c\text{-}C_6H_{11})_2]_2$.

[b] ^{13}C-NMR chemical shift.

[c]




η^3-allyl(C_3R_5)


η^2-metallacyclo-butane (C_3R_6)


η^2-metallacyclo-butene (C_3R_4)


η^2-metallacyclo-butadiene (C_3R_3)

The η^3-C_3R_3 skeleton configuration is severely bent to 145 ~ 155°. All the known title compounds have one C_c–C_t distance in the region between short double bonds and long triple bonds (1.22–1.29 Å), and the other in the range of long double bonds (1.32–1.41 Å), clearly showing the resonance structure between allenyl and propargyl. The M–C_c bond distances (2.11–2.44 Å) are between those of the two M–C_t bonds. The M–CR_2 bonds (2.23–2.56 Å) are longer than those of the M–CR′ bonds (1.98–2.32 Å) which are well correlated with the corresponding $J_{\text{C Pt}}$ values. Important structural data are also listed in Table 1.

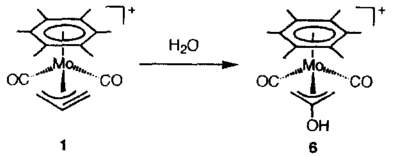
3. Addition reactions of η^3-allenyl/propargyl complexes

3.1. *Reactions with Group VIA nucleophiles*

3.1.1. *Hydroxylation*

Although the development of diverse syntheses for mononuclear η^3-allenyl/propargyl complexes has been rapid, reactivity studies for such species are only now appearing. In a general sense, these complexes are susceptible to nucleophilic addition mainly at the central carbon of the organic ligands, but also at the metal centers in a few cases. Complexes with the unsubstituted η^3-C_3H_3 ligand are the most reactive and demonstrate an extraordinarily broad reaction scope.

The molybdenum complex **1** shows activity toward water addition to give a η^3-2-hydroxyallyl product $[(Me_6C_6)Mo(CO)_2(\eta^3\text{-}CH_2C(OH)CH_2)]^+$ (**6**) (Eq. 13). In the platinum system, although solid **3a** may be preserved in a dry nitrogen atmosphere, it deteriorates rapidly in air. The stoichiometric reactions of **3a** with water at 25°C instantaneously produce a η^3-2-hydroxyallyl cation $[Pt(PPh_3)_2(\eta^3\text{-}CH_2C(OH)CH_2)]^+$ (**7a**) and a diplatina-η^6-diallyl ether dication $\{[(PPh_3)_2Pt(\eta^3\text{-}C_3H_4)]_2O\}^{2+}$ (**8a**) with relative yields of 4:1. When the same reaction was carried out below 0°C, the relative yields of **7a** versus **8a** change to 1:4. This is presumably due to the mobility and solubility of water in methylene chloride which drop markedly below the freezing point. The hydroxyallyl complex therefore, first formed is allowed to react with **3a** (vide supra) [19a]. A deliberate reaction containing equimolar amounts of **3a** and **7a** under strictly anhydrous conditions indeed affords **8a** quantitatively. The reaction of **3b** and a large excess of water also produces diplatinadially-ether **8b** [19b]. However, the corresponding hydroxyallyl complex **7b** was not detected, presumably it would rapidly react with available **3b**. Deprotonation of **7a** or treatment of **8a** or **8b** with OH^- or OR^- will lead to the formation of η^3-oxatrimethylenemethane (η^3-OTMM) complexes, $Pt(PPh_3)_2(\eta^3\text{-}CHRCOCH_2)$ (**9**) (Eqs. 14, 15) [8b,24].



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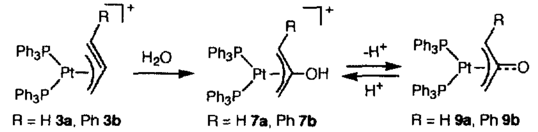

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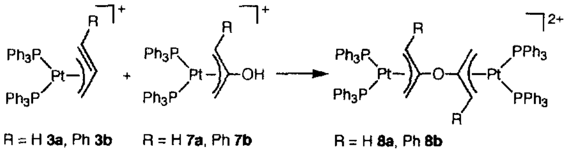
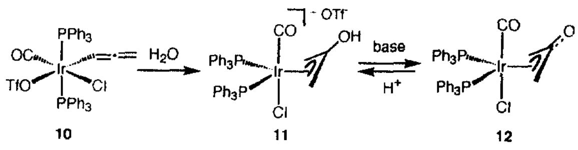


(15)

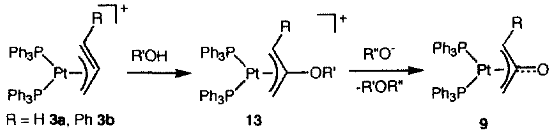
Similar hydroxylation of metal η^1-allenyls is also possible, although it is still not clear whether the formation of η^3-allenyl/propargyl intermediates take place during the reaction course. Addition of water to $Pt(Cl)(PPh_3)_2$-(η^1-$CHCCH_2$) is much slower than to **3a**. However, the octahedral iridium complex (*OC*-6-42)-$Ir(Cl)_2(PPh_3)_2(CO)$(η^1-$CHCCH_2$) is inert to water addition under similar conditions. By contrast, the labile iridium triflate derivative, (*OC*-6-42)-$Ir(Cl)(PPh_3)_2$-(OTf)(CO)(η^1-$CHCCH_2$) (**10**) readily reacts with water to give {$Ir(Cl)(PPh_3)_2(CO)$-[η^3-$CH_2C(OH)CH_2$]}(OTf) (**11**) and $Ir(Cl)(PPh_3)_2(CO)$[η^3-$CH_2C(O)CH_2$] (**12**) (Eq. 16), indicating that the pre-coordination of water has to be crucial [25]. Furthermore, the addition rates to complex **10** are significantly accelerated when excess water is used. Curiously, the η^3-allenyl/propargyl palladium complexes **4** are completely inert to water.



(16)

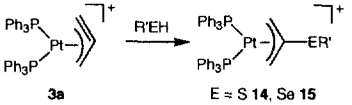
3.1.2. Organochalcogenoxylation

The reaction of Eq. 15 suggests that cationic η^3-allenyl/propargyl complexes are subject to alkoxylation. Indeed, complexes **3a** and **3b** react not only with a variety of alcohols but also poor nucleophiles of phenol derivatives to give, respectively, the central-carbon-substituted alkoxy- and phenoxy-η^3-allyl complexes {$Pt(PPh_3)_2$[η^3-$CHRC(OR')CH_2$]}$^+$ (**13**) [13b,19,26]. For synthetic purposes, excess nucleophiles, especially for the weak ones, are often needed to suppress water addition. Treating **13** with strong base such as RO^- also gives η^3-OTMM (Eq. 17) [26b].



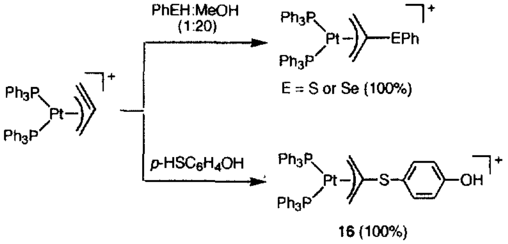
(17)

To extend the bond-forming scope to other chalcogen atoms, the construction of C–S and C–Se bonds between **3a** and thiol, thiophenol, or selenophenol succeeds to yield thioxy- and selenoxy-allyl complexes $\{Pt(PPh_3)_2\text{-}[\eta^3\text{-}CH_2C(ER')CH_2]\}^+$ (E = S **14**, Se **15**), respectively (Eq. 18). These reactions which readily overwhelm water addition do not need excess nucleophiles. In fact, extra REH would lead to the formation of *cis*-$Pt(ER)_2(PPh_3)_2$ as by-products.



(18)

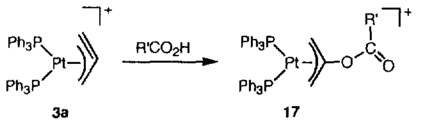
According to the competitive experiments, addition of either PhSeH or PhSH to **3a** overwhelmingly exceeds methoxylation even when a 20-fold excess of methanol is used. PhSeH is more reactive than PhSH. The reaction of **3a** with *p*-HSC_6H_4OH results in exclusive C–S bond-formation, leading to $\{Pt(PPh_3)_2[\eta^3\text{-}CH_2C(SC_6H_4OH)CH_2]\}^+$ (**16**) (Eq. 19). All these results suggest that the nucleophilicity of the added substance is essential to the addition reactions of the η^3-allenyl/propargyl complexes. On the other hand, the relative rates of adding R'OH to **3a** are MeOH:EtOH:^{i}PrOH:^{t}BuOH:PhOH = 70:40:23:4:1, indicating the influence of steric effect (vide supra).



(19)

3.1.3. Addition with weak nucleophiles

The feasible phenoxylation of **3a** indicates that the reactivity of η^3-allenyl/propargyl toward addition might not be solely decided by the nucleophilicity of the added species. The addition reactions of **3a** are also attained with carboxylic acids RCO_2H, $ArCO_2H$ and CX_3CO_2H (X = F, Cl). The resulting acyloxylation of η^3-allenyl/propargyl yields new acyloxyallyl complexes $\{Pt(PPh_3)_2[\eta^3\text{-}CH_2C(OCOR')CH_2]\}^+$ (**17**) (Eq. 20) [27]. Electrophilic addition of organic halides to η^3-OTMM complexes **9** affords an alternative methodology for the synthesis of central-carbon-substituted η^3-allyl complexes (Eq. 21). In contrast to conventional transition metal allyl species which incline to suffer nucleophilic attack at the terminal carbon, alkoxy- and acyloxy- allyl complexes are subject to nucleophilic substitution at the central carbon (Eqs. 22–24), presumably undergoing an addition–elimination mechanism. Such a reactivity certainly allows one to provide new features to organic synthesis [44].



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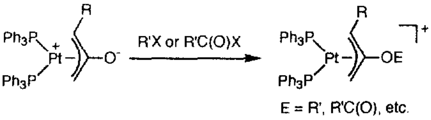

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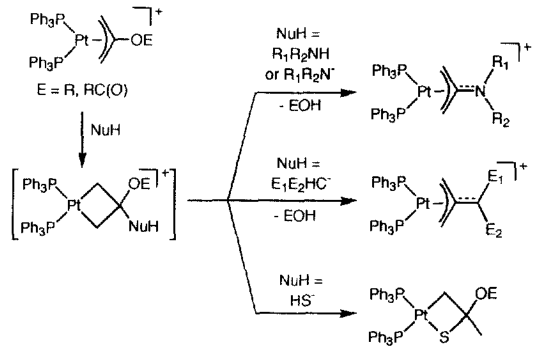
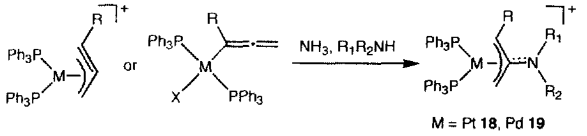


(22–24)

3.2. Reactions with Group VA nucleophiles

3.2.1. Amination and amidation

Regioselective addition of ammonia, primary or secondary amines, aniline and its derivatives to cationic η^3-allenyl/propargyl complexes of Pt or Pd **3** is also feasible. Similar reactions of neutral η^1-allenyl complexes of Pt or Pd are successful but relatively sluggish. The common products are cationic complexes of N-protonated, N-alkylated, and N-arylated η^3-azatrimethylene-methane (η^3-NTMM) $\{M(PPh_3)_2[\eta^3\text{-}CH_2C(NRR')CH_2]\}^+$ (M = Pt **18**, Pd **19**), wherein the broad spectrum of attempted substituents comprise R = H R' = H, Me, Et, ^{i}Pr, ^{t}Bu, c-C_6H_{11}, Ph, CH_2CH_2OH, R = R' = Et, c-C_3H_6 (azetidine), Ph, R = Me R' = Ph (Eq. 25) [28]. Hydrazine undergoes double addition with **3a** to give metallapyrazoline $[(PPh_3)_2\overline{Pt(CH_2CMeNNH_2)}]^+$ (**20**) (Eq. 26) [29].



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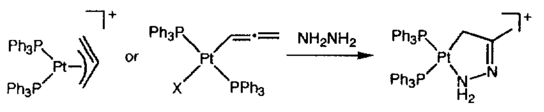
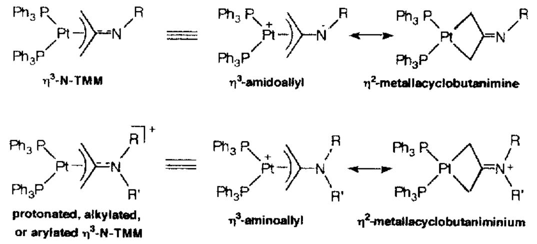
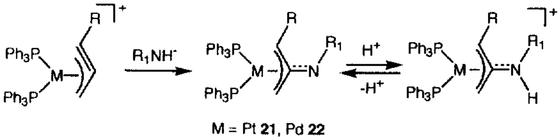


20 (26)

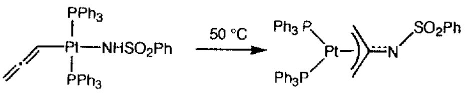
Addition reactions of amides $R'NH^-$ to **3** provide the synthesis of neutral η^3-NTMM complexes $Pt(PPh_3)_2[\eta^3\text{-}CHRC(NR')CH_2]$ (M = Pt **21**, Pd **22**). The η^3-NTMM complexes can also be prepared by reaction of η^3-allenyl/propargyl complexes with primary amine, followed by deprotonation [8b,19b,28]. As to weak amines such as $TsNH_2$ and $PhSO_2NH_2$ which are not reactive towards **3**, their corresponding amides may achieve addition. Protonation of the η^3-NTMM complexes compensates to afford the products of amination (Eq. 27). Another alternative synthetic route for the tosylate derivative, $Pt(PPh_3)_2\text{-}[\eta^3\text{-}CHRC(NTs)CH_2]$ is via the reaction of η^3-OTMM and TsNCO [44a]. The η^3-NTMM complexes are isoelectronic with the η^3-OTMM complexes, and make a class of new organometallic species which may be envisaged to have intermediary structural characteristics between η^3-2-amidoallyl and η^2-metallacyclobutanimine.





(27)

The reactions of η^1-allenyl complexes with amide have been further examined by treating *trans*-$Pt(PPh_3)_2(OAc)(\eta^1\text{-}CHCCH_2)$ with $PhSO_2NH^-$. A *trans*-η^1-allenyl(amido) complex *trans*-$Pt(PPh_3)_2(NHSO_2Ph)(\eta^1\text{-}CHCCH_2)$ (**23**) was found to form first and transform subsequently into $Pt(PPh_3)_2(\eta^3\text{-}CH_2C(NSO_2Ph)CH_2]$ (Eq. 28). Adding diphenylphosphinoethane (dppe) to *trans*-$Pt(PPh_3)_2(Cl)(\eta^1\text{-}CHCCH_2)$ first gives a *cis*-η^1-allenyl(amido) complex *cis*-$Pt(dppe)(NHSO_2Ph)(\eta^1\text{-}CHCCH_2)$ (**24**) which then produces *cis*-$Pt(dppe)\text{-}[\eta^3\text{-}CH_2C(NSO_2Ph)CH_2]$ upon heating (Eq. 29).



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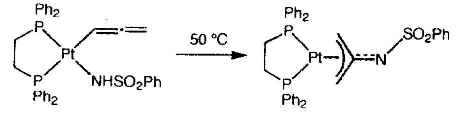

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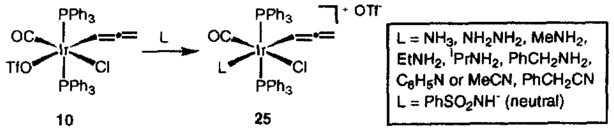
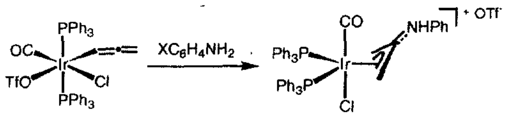
(29)

In the octahedral iridium systems, the reactions of (*OC*-6-42)-Ir(Cl)-(PPh$_3$)$_2$(OTf)(CO)(η^1-CHCCH$_2$) (**10**) and amino compounds such as NH$_3$, NH$_2$NH$_2$, MeNH$_2$, EtNH$_2$, ^{i}PrNH$_2$, and PhCH$_2$NH$_2$, PhSO$_2$NH$^-$, C$_6$H$_5$N or MeCN, PhCH$_2$CN give rise to substitution, leading to {*OC*-6-42-Ir(Cl)-(PPh$_3$)$_2$(L)(CO)(η^1-CHCCH$_2$)}(OTf) (**25**) (Eq. 30). On the other hand, the aniline derivatives XC$_6$H$_4$NH$_2$ (X = F, NO$_2$, MeO, H, Me) achieve the addition to **10**, yielding arylated η^3-NTMM products {Ir(Cl)(PPh$_3$)$_2$(CO)[η^3-CH$_2$C(NHC$_6$H$_4$-X)CH$_2$)}(OTf) (**26**) (Eq. 31) [30]. This also indicates that the coordination of nucleophiles is a prerequisite for the addition to the η^1-allenyl complexes. Besides, N–H bond activation by metal has to be crucial to addition too.



10 **25**

(30)

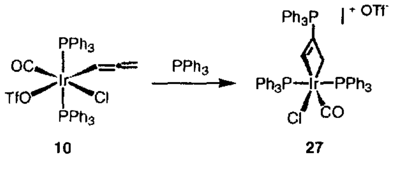


10 **26**

(31)

3.2.2. Reactions with tertiary amines and phosphines

The reaction between **10** and PPh$_3$ results in C–P coupling, leading to an iridacyclobutene {(Cl)(PPh$_3$)$_2$(CO)Ir[CH$_2$C(PPh$_3$)CH]}(OTf) (**27**) (Eq. 32) as sole product [31]. Similar reactions are also observed for η^3-allenyl/propargyl rhenium and platinum complexes **2** and **3**, but not for *trans*-Pt(PPh$_3$)$_2$(X)(η^1-CHCCH$_2$) and (*OC*-6-42)-Ir(Cl)$_2$(PPh$_3$)$_2$(CO)(η^1-CHCCH$_2$).

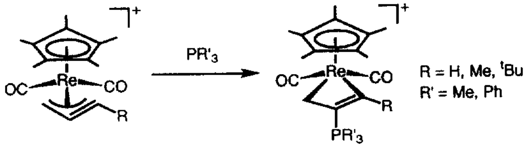


10 **27**

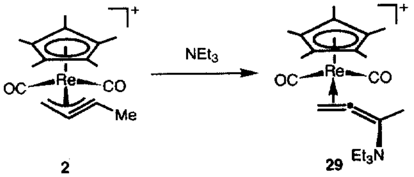
(32)

The reactions of [Cp*Re(CO)$_2$(η^3-H$_2$CCCR)]$^+$ (R = H, Me, ^{t}Bu) and phosphines yield rhenacyclobutene adducts {Cp*(CO)$_2$Re[CH$_2$C(PR'$_3$)CR]}$^+$ (R' = Me, Ph **28**) (Eq. 33) [32]. However, the reaction of NEt$_3$ with **2** leads to an η^2-allene complex {Cp*Re(CO)$_2$[η^2-H$_2$CCCR(NEt$_3$)]}$^+$ (**29**) by adding the amino group at a carbon terminus (Eq. 34), indicating regiochemistry for nucleophilic addition at the central carbon is not the only possibility. Similar reactivity also occurs with the molybdenum η^3-allenyl/propargyl analog **1**, with which mixed products of phosphinoallyl and allene complexes are observed [10a]. The η^3-allenyl/propargyl platinum complex **3a** reacts with either NEt$_3$ or PPh$_3$ to form the cationic platinacyclobutenes

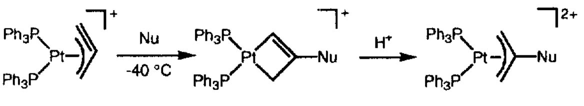
$\{(PPh_3)_2Pt[CH_2C(Nu)CH]\}^+$ ($Nu = NEt_3$ **30** PPh_3 **31**) exclusively, at −40°C (Eq. 34). Reactions of the platinum system are sensitive to elevated temperature or excess nucleophile which would destroy the products. The presence of acid transforms metallacyclobutenes into allyl species from metallacyclobutenes (Eq. 35) [31].



2 **28** (33)

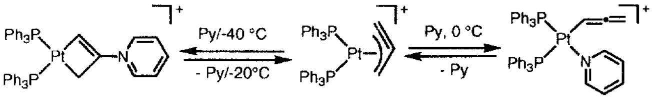


2 **29** (34)

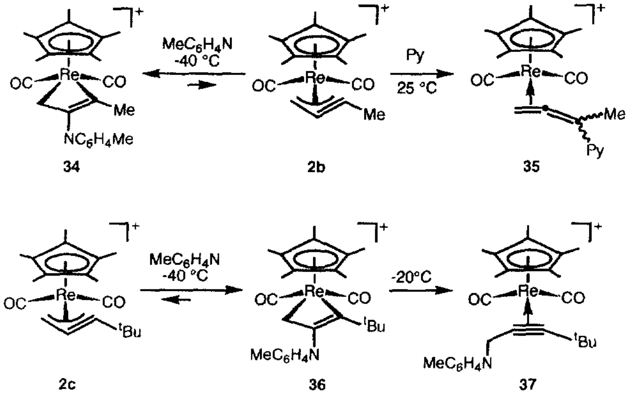


3a Nu = NEt3 **30**, PPh3 **31** (35)

Reactivity with pyridine shows some mechanistic similarity between **2** and **3**. The platinum complex **3a** can undergo nucleophilic attack by pyridine either at the central carbon to give $\{(PPh_3)_2Pt[CH_2C(Py)CH]\}^+$ (**32**) or at the metal center to give *cis*-$[Pt(PPh_3)_2(Py)(\eta^1\text{-}CHCCH_2)]^+$ (**33**) (Eq. 36). Complex **32** is the kinetic product and **33** is thermodynamically more favored. Both products may lose pyridine to revert to **3a** which can be hydrolyzed to the hydroxyallyl, η^3-O-TMM, and η^6-diallyl ether complexes if moisture is present. To rhenium complexes **2b** and **2c**, the pyridine derivatives also kinetically add to the central carbon to give rhenacyclobutene complexes (**34**, **36**) at low temperature. Upon warming, rhenacyclobutenes dissociates pyridine which, however, readded at the terminal site to give either an allene (**35**) or an alkyne complex (**37**), respectively (Eqs. 37, 38).



32 **3a** **33** (36)



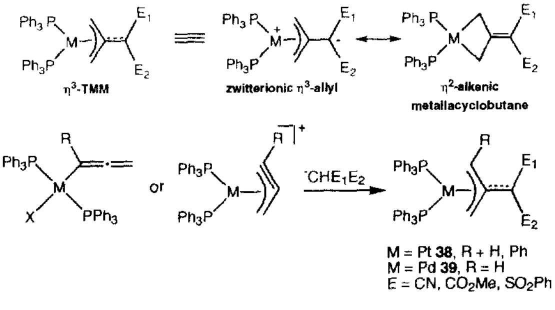
(37, 38)

3.3. Reactions with Group IVA nucleophiles

3.3.1. Reaction with carbanions

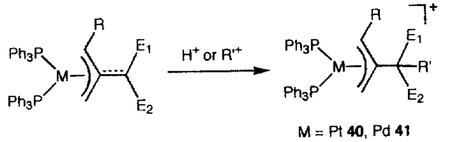
Successful addition of electron donors involving the elements in the lower periodic table to the η^3-allenyl/propargyl complexes indicate that such new organometallic species are reactive to soft as well as hard nucleophiles. The endeavor for C–C bond formation with allenyl and/or propargyl complexes is not only a logical extension of reaction scope, but also intriguing for organic synthetic purposes.

Casey and coworkers led in this realm, with the reactions of **2** and acetylides, organic cuprates, or carbanions, from which rhenacyclobutenes again were the products [11,32]. Similar reactions of the palladium and platinum complexes with carbanions exhibit distinguishable results. Synthesis of zwitterionic η^3-trimethylenemethane (η^3-TMM) complexes of Pd and Pt $M(PPh_3)_2(\eta^3\text{-}CHRC(CE_1E_2)CH_2)$ (E_1, E_2 = CN, CO_2Me, SO_2Ph, etc.; M = Pt R = H, Ph **38**; M = Pd R = H **39**) has been accomplished by adding carbanions $Na[CH(E_1)(E_2)]$ to either the η^1-allenyl or η^3-allenyl/propargyl complexes (Eq. 39) [8b,33]. The η^3-TMM complexes which are similar to the aforementioned η^3-OTMM and η^3-NTMM complexes exhibit a resonance structure between zwitterionic η^3-allyl and alkenic metallacyclobutane forms. Spectral evidence for such structures were first acquired mainly using NMR techniques, and then single-crystal X-ray crystallography offered unequivocal confirmation.



(39)

The zwitterionic character of η^3-TMM complexes is also supported by their chemical behavior. Protonation or alkylation of **38** or **39** leads to the central-carbon-substituted η^3-hydrocarbylallyl cations $\{M(PPh_3)_2[\eta^3\text{-}CHRC(CR'E_1\text{-}E_2)\text{-}CH_2]\}^+$ ($R = H$, Ph; $R' = H$, Me, Et; M = Pt **40**, Pd **41**) (Eq. 40). When carbon enolates react with palladium η^3-allenyl/propargyl or palladium η^1-allenyl complexes, hydrofurans were produced via the formation of Pd-η^3-TMM. Such results afford direct evidence that Pd-η^3-TMM are the key intermediates in Pd-catalyzed addition–cyclization reactions of propargyl carbonates and carbon nucleophiles (Eq. 41) [34].



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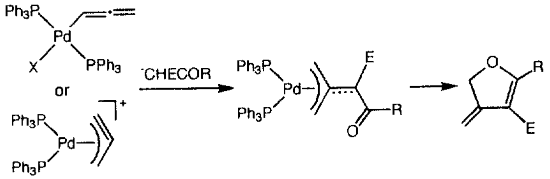
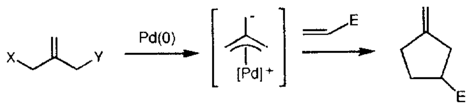


(41)

In addition, zwitterionic Pd-η^3-TMM complexes have also been proposed as fleeting intermediates in Pd-catalyzed [3 + 2] cycloaddition reactions (Eq. 42) [35]. Trost et al. have endeavored to design a variety of organic bifunctional conjunctive reagents, reacting with Pd(0) to provide Pd-η^3-TMM complexes in situ, but no success in isolating these species [36]. Theoretical and mechanistic studies suggest that Pd-η^3-TMM species should be energetic and may exhibit distinguishable chemistry from the better-studied η^4-TMM complexes [37]. Although the EWG-stabilized Pd-η^3-TMM are not as reactive as the unsubstituted one, they still undergo coupling with strong olefinic electrophiles such as tetracyanoethylene (TCNE) or maleic anhydride (MA) to form the highly substituted products of [3 + 2] cycloaddition (Eqs. 43, 44). A similar reaction between Pt-η^3-TMM and TCNE was also reported (33b). These cyclopentanoids can not be obtained by the catalytic process, for good π-acids as TCNE and MA would react with Pd(0) before Pd-η^3-TMM is formed.



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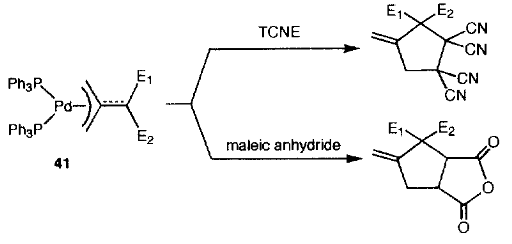
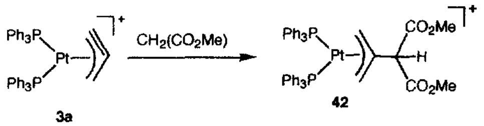


(43, 44)

3.3.2. Aromatic electrophilic substitution

Preliminary studies have shown that the cationic η^3-allenyl/propargyl platinum complex **3a** can curiously react with alkane (Eq. 45), alkyne (Eq. 46), and silane (Eq. 47) to yield various η^3-allyl products (**42**–**44**) [13]. Successful expedition for the addition reactions of **3a** with soft nucleophiles has led to research into other electron-rich systems. One of the fundamental strategies to achieve C–C coupling between unsaturated hydrocarbons is via Friedel–Crafts reactions [38]. In the typical examples, a Lewis acid is required to create a carbon electrophile which results in aromatic substitution. To use organometallic electrophiles for such a purpose is attractive because the metal may activate the ligated organic moiety and facilitate the carbon–carbon bond formation in a new manner [39,40]. The η^3-allenyl/propargyl complexes conduct the addition of the aromatic C–H bonds across the C–CH bond of the C_3H_3 moiety [41].



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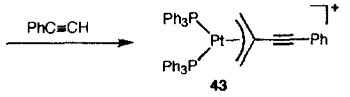

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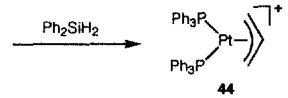
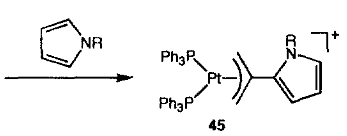


(47)

Hydropyrrolylation of **3a** is accomplished by directly reacting **3a** with pyrrole or N-methylpyrrole in a nitrogen atmosphere. As the electrophilic attack on pyrrole normally occurs at the 2-position, the C–C coupling takes place exclusively between the central carbon of C_3H_3 and the 2-pyrrolyl carbon, thereby generating the central-carbon-substituted η^3-2-pyrrolylallyl complexes $\{Pt(PPh_3)_2[\eta^3\text{-}CH_2C(2\text{-}C_4H_3NR)CH_2]\}^+$ (**45**) (Eq. 48). In the reaction of **3a** with indole, the insertion of C_3H_3 into the 3-indolyl C–H bond leads to the formation of $\{Pt(PPh_3)_2[\eta^3\text{-}CH_2C(3\text{-}indolyl)CH_2]\}^+$ (**46**) (Eq. 49). The addition of 3-methylindole to **3a** yields formation of $\{Pt(PPh_3)_2[\eta^3\text{-}CH_2C(2\text{-}3\text{-}methylindolyl)CH_2]\}(BF_4)$ (**47**) at a relatively slow rate (Eq. 50).



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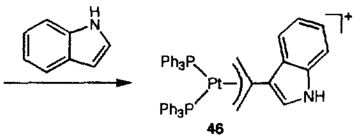
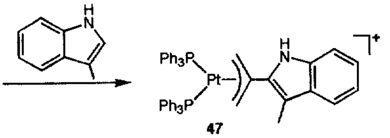


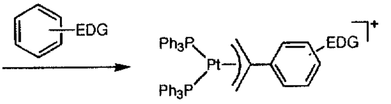
(49)



47

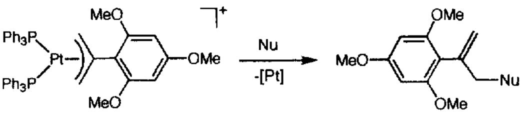
(50)

As to the aryl system, complex **3a** can undergo addition of the aryl C–H bonds of PhNMe$_2$, dimethoxy-, or trimethoxybenzene to form 2-η^3-arylallyl complexes {Pt(PPh$_3$)$_2$[η^3-CH$_2$C(Ar)CH$_2$]}(BF$_4$) (Ar = 4-Me$_2$NC$_6$H$_4$ **48**, 2,4-(MeO)$_2$C$_6$H$_3$ **49**, 2,4,6-(MeO)$_3$C$_6$H$_2$ **50**) (Eq. 51) with regioselectivity of conventional electrophilic aromatic substitution. The reactions between **3a** and the less electron-rich arenes such as benzene, toluene, xylene, or anisole, etc. do not take place under the same conditions. Nucleophilic addition of ^{n}Bu$_4$NBH$_4$, NaSPh, or Na[CH(SO$_2$Ph)$_2$] at the terminal carbon of **50** gives CH$_2$C[2,4,6-(MeO)$_3$C$_6$H$_2$]CH$_2$Nu (**51**) (Eq. 52). With respect to the arenes, the overall transformation achieves vinylation of arenes, which provides the same kind of products as result from the Heck or Stille reactions of vinylic arylation [42].



EDG = 4-NMe$_2$ **48**
2, 4-dimethoxy **49**
2,4,6-trimethoxy **50**

(51)



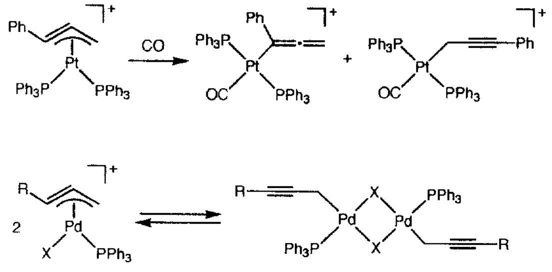
51

(52)

4. Mechanisms of nucleophilic addition of allenyl and/or propargyl complexes

4.1. Addition to metal η^1-allenyl requires preceding coordination of nucleophile

Wojcicki and Kurosawa have shown that the η^3-allenyl/propargyl complexes may release their π-interaction to form either η^1-allenyl or η^1-propargyl complexes [5c,13a,14b] (Eqs. 53, 54). The η^1-allenyl complexes are also subject to nucleophilic addition. The formation of (η^1-allenyl)amido platinum complexes **23** and **24** and their transformation into the η^3-NTMM products support the view that hydroamination of the η^1-allenyl complexes likely involves a preceding amide coordination step [28]. The octahedral η^1-allenyl iridium **10** undergoes substitution of a variety of amino compounds for the triflate ligand [30]. However, the reactions of **10** and aniline derivatives give products of hydroanilination. Detailed studies found that when equimolar amounts of **10** and aniline react at 243 K, an aniline-ligated complex [*OC*-6-42-Ir(Cl)(PPh_3)$_2$(NH_2Ph)(CO)(η^1-$CHCCH_2$)]-(OTf) (**25an**) was first formed. Adding benzylamine (one equivalent) followed by raising the reaction temperature to 273 K resulted in a mixture of the benzylamine-coordinated complex (**25bz**) and the N-phenylated η^3-NTMM complex **26** in 1:1.3 relative yields. Complex **25bz** did not cause the formation of corresponding N-benzylated η^3-NTMM product. However, the mixing of equimolar amounts of aniline and **25bz** at 25°C also resulted in the formation of **26** to 96% yields, basically at the expense of **25bz**. Apparently, ligand substitution is reversible, and the equilibrium favors the better electron-donating **25bz** more than **25an** (Eq. 55).



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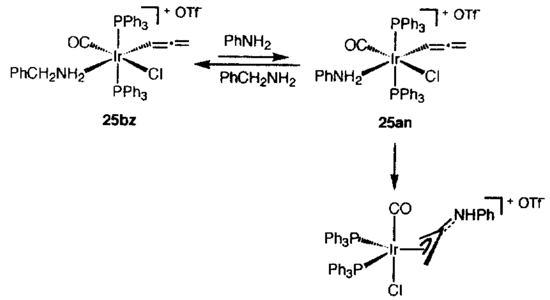
(53, 54)



25bz

25an

26

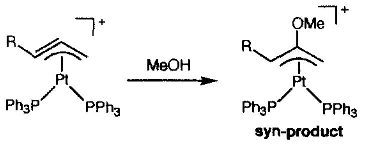
(55)

The reaction course from **25an** to **26** is not explicit. The reactivity discrepancy between **25an** and **25bz** suggests that the feasibility of N–H bond cleavage is crucial, in addition to the nucleophilicity of added groups [43]. Similar phenomena were also displayed by water and alcohol which have relatively low basicity and nucleophilicity, but are readily added to **10**, whereas ammonia, amide, as well as amines of good nucleophilcity and basicity are inert to addition. One may conceive that coordination of the amino group allows the metal to play a prominent role to the activation of the N–H bond as well as the formation of the C=N bond, and thereby conveys selectivity into such a chemical transformation.

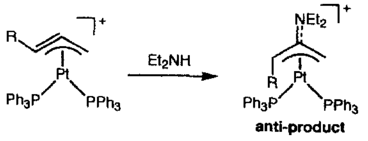
4.2. Direct external nucleophilic attack at the η^3-allenyl/propargyl central carbon

4.2.1. N–H addition versus O–H addition

None of the reactions of N–H addition and O–H addition have shown the detection of metallacyclobutene intermediate. However, protonation of the isolated metallacyclobutenes leads to the formation of η^3-allyl complexes [22f,31]. Wojcicki with his phenyl-substituted η^3-allenyl/propargyl complexes could observe that alkoxylation and amination showed different stereochemistry in the resulting η^3-allyl complexes, a syn-product for the former (Eq. 56) and an anti-product for the latter reaction (Eq. 57) [13b]. The same stereochemistry of addition was observed by Casey and his coworkers in the reaction of D_2O with $[C_5Me_5(CO)_2Re(\eta^3\text{-}HCCCH_2)]^+$. Clean formation of 2-hydroxyallyl $\{C_5Me_5(CO)_2Re[\eta^3\text{-}HDCC(OD)CH_2]\}^+$ (**53**) with regio- and stereospecific isotope-addition was isolated (Eq. 58). The added deuterium on the allyl terminal carbon only appears at the anti-position.



(56)



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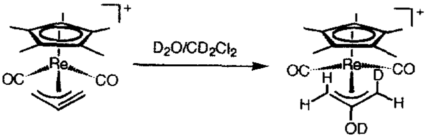
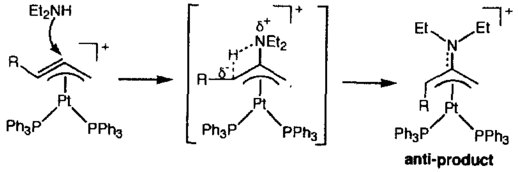


53

(58)

The anti-product from amination may be explained by nucleophilic attack of amine at the central carbon of η^3-$RCCCH_2$ with an essentially synchronous proton transfer to the CR carbon (Eq. 59). In contrast, water or alcohol addition undergoes nucleophilic attack at the η^3-allenyl/propargyl central carbon to form a neutral metallacyclobutene intermediate **I**. The following protonation at metal will give a (hydrido)metallacyclobutene **II**. Transfer of the proton to the CR carbon away from the alkoxy group would afford the anti-labeling η^3-allyl product (Eq. 60). The relative rates for the addition of R'OH to **3a** indicate the mild influence of a steric effect which may be elucidated by protonation at metal with use of ROH_2^+.



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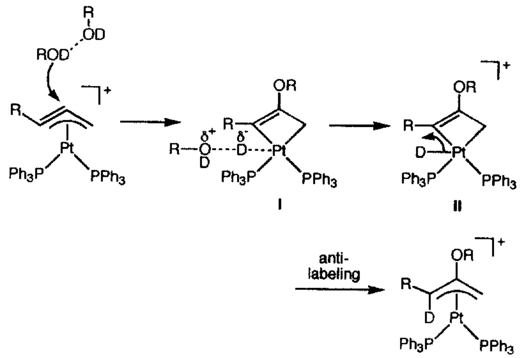
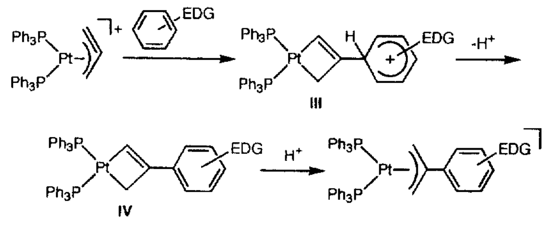


(60)

4.2.2. Aromatic C–H addition

The reactions shown in Eqs. 46–51 reveal regiochemistry of electrophilic aromatic substitution. To seek further evidence for such a mechanism, a crossover labeling experiment has been carried out. A sample of 1,3,5-$(MeO)_3C_6D_{3-n}H_n$ ($n = 0$, 1) with d_2:d_3 = 22:78 was mixed with an equimolar amount of 1,3,5-$(MeO)_3C_6H_3$. The resulting 1,3,5-trimethoxybenzene with a labeling distribution of d_0:d_2:d_3 = 50:11:39 was reacted with **3a** followed by treatment with NaSPh. The NMR spectra showed the formation of 2-$CH_2C[2,4,6-(MeO)_3C_6H_2]CH_2(SPh)$ (**51**) with deuterium appearing at the aryl ring and the allyl terminal carbon but without stereospecificity. The mass spectroscopy provides the deuterium distribution of intermolecular hydrogen scrambling. A mechanism involving electrophilic addition (intermediate **III**) and formation of metallacyclobutene **IV** which undergoes external protonation to yield the allyl product may explain these reactions (Eq. 61).



(61)

Comparison with the Friedel–Craft aromatic substitution reactions which require an external Lewis acid promoter, the unique bonding of the η^3-allenyl/propargyl complexes intrinsically confers sufficient electrophilicity at the central carbon of the ligands. As a result, the η^3-allenyl/propargyl ligand reveals remarkably high reactivity as well as subtle chemical selectivity towards various aromatics.

5. Concluding remarks

The cationic mononuclear η^3-allenyl/propargyl complexes exhibit new non-classical organometallic bonding features and the activity of potent carbon electrophiles which appeal to direct external nucleophilic attack at the central carbon. The reactions of nucleophilic addition of the title complexes provide pragmatic synthetic access to new organometallic species of various central-carbon-substituted η^3-allyls, η^3-heterotrimethylenemethanes, γ-substituted η^3-trimethylenemethanes, η^2-allenes, and metallacyclobutenes. The η^3-allenyl/propargyl ligands may release the π-interaction to transform into either η^1-allenyl or η^1-propargyl complexes. The linear η^1-allenyl complexes are also subject to regioselective nucleophilic addition at the central carbon of the ligand; however, this requires the preceding coordination of nucleophiles.

Acknowledgements

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