

Reactions of electrophilic transition metal cations with olefins and small ring compounds. Rearrangements and polymerizations

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Abstract

The reactivity of the cationic, weakly ligated, transition metal compounds, $[\text{Pd}(\text{MeCN})_4](\text{BF}_4)_2$ (**1**); $[\text{M}(\text{MeCN})_6](\text{BF}_4)_2$, ($\text{M} = \text{Ni}$, **2**; Co , **3**); $[\text{M}(\text{NO})_2(\text{MeCN})_4](\text{BF}_4)_2$, ($\text{M} = \text{Mo}$, **4**; W , **5**), vis-à-vis olefins and strained ring compounds was studied. A number of these species were observed to form a charge-transfer complex with tetra-*p*-anisylethylene. These compounds were also found to catalyze the skeletal rearrangement and polymerization of appropriately substituted olefins and cyclopropanes. These reactions appear to be initiated by the electrophilic (heterolytic) cleavage of either the π -bond of the olefin or a strained C–C σ -bond of the small ring compound.

Introduction

The chemistry of electron-rich transition metal centers has been studied extensively in recent years, and many of the characteristic reactions are, by now, well-understood. The one reaction that appears to dominate this chemistry is oxidative addition (eq. 1) [1], and the propensity to undergo this reaction increases with increasing electron density on the metal.



In contrast, the mechanistic aspects of the chemistry of electrophilic metal ions, especially those belonging to the later transition metals, have received less attention despite literature precedents that indicate that the important reaction pathways for this class of compounds are very different from those observed for electron rich metals. For example, the heterolytic cleavage of bonds appears to be the dominant reaction with electrophilic metals (eq. 2).



Table 1 [3]

Comparison of electrophilicity of transition and main group metal ions

Ion	Promotion energy (eV) ^a	Electron affinity (eV)
Rh ^I	1.6	7.31
Ir ^I	2.4	7.95
Pd ^{II}	3.05	18.56
Pt ^{II}	3.39	19.42
Cu ^I	8.25	7.72
Ag ^I	9.94	7.59
Zn ^{II}	17.1	17.96
Cd ^{II}	16.6	16.9
Hg ^{II}	12.8	18.75

^a $nd^x \rightarrow nd^{x-1}(n+1)p^1$.

In this paper, we describe the full details of the rearrangement and polymerization of olefins and small ring compounds by several electrophilic transition metal cations [2]. As we shall demonstrate, these reactions are initiated by the electrophilic (heterolytic) cleavage of either the π -bond of the olefin or a strained C–C σ -bond of the small ring compound. Furthermore, as might be expected, the propensity to undergo these reactions decreases with increasing electron density of the metal.

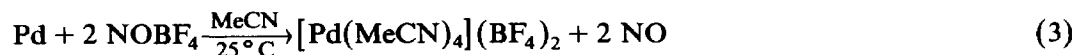
Before examining the organic chemistry of transition metal electrophiles, it is worthwhile to compare them with the traditional main-group Lewis acids. As Table 1 illustrates [3], the electron affinity of Pd^{II} is comparable to those of Zn^{II} and Hg^{II}. However, the Pd^{II} ion has a smaller electron promotion energy and this results in stronger initial binding with organic substrates like olefins because of more efficient back-bonding. This mode of interaction is energetically unfavorable for most common Lewis acids, and this constitutes the principal difference between transition metal electrophiles on one hand and the more traditional main-group electrophiles on the other.

Results and discussion

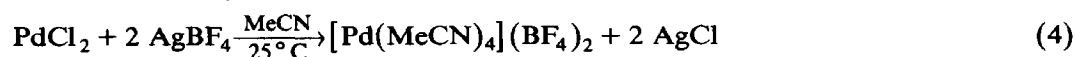
A. Synthesis of the transition metal compounds

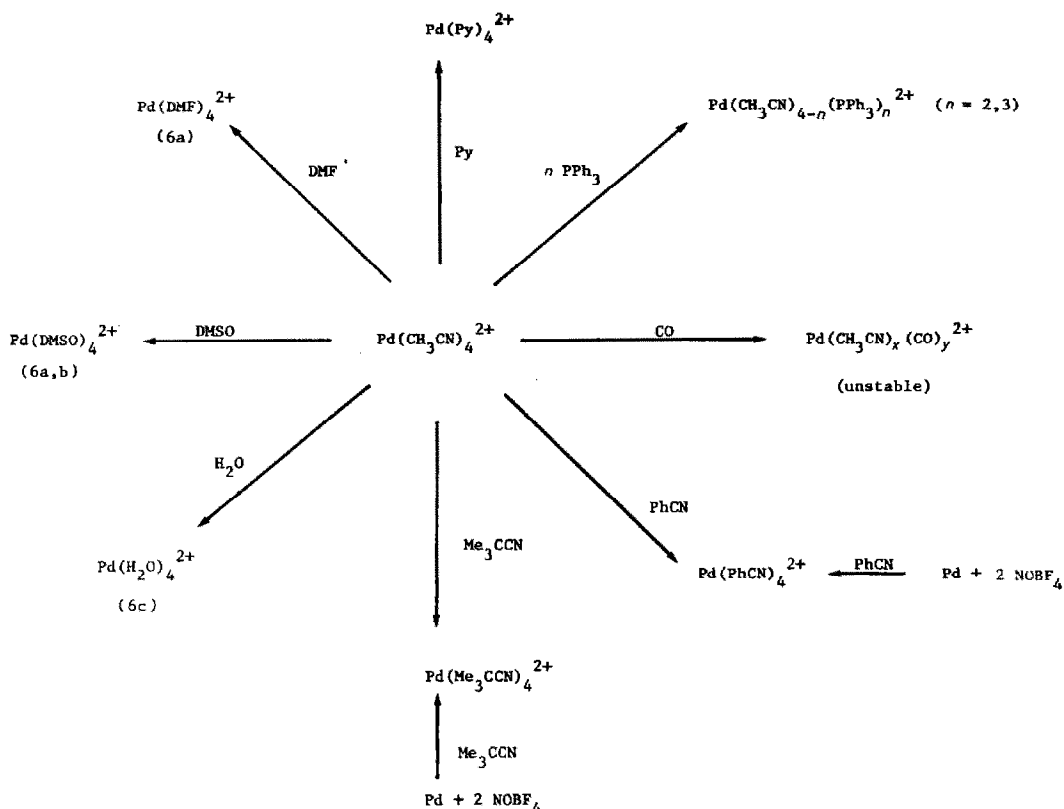
In order to study the reactivity of the transition metal electrophiles as a function of the central metal ion, we have examined the reactivity pattern of the following series of complexes: [Pd(MeCN)₄](BF₄)₂ (**1**); [M(MeCN)₆](BF₄)₂, (M = Ni, **2**; Co, **3**); [M(NO)₂(MeCN)₄](BF₄)₂, (M = Mo, **4**; W, **5**). These are all cationic complexes incorporating the weakly ligating MeCN ligand and having the non-coordinating BF₄⁻ counteranion. They are air-stable, moisture-sensitive solids that are readily soluble in polar solvents such as, MeCN and MeNO₂, but are insoluble in less polar media.

Compound **1** was usually synthesized by the oxidation of metallic Pd by NOBF₄ in MeCN (eq. 3) [4]. An alternative, less clean, method of synthesis involved the



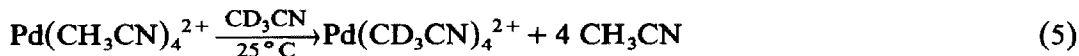
reaction of PdCl₂ with two equiv. of AgBF₄ in MeCN (eq. 4). In its IR spectrum, **1**





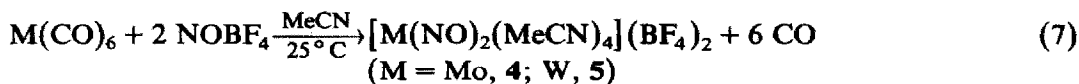
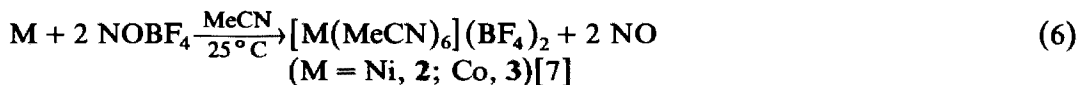
Scheme 1. Substitution reactions of $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$.

exhibited a $\bar{\nu}(\text{C}\equiv\text{N})$ band at 2335 cm^{-1} , which was 81 cm^{-1} higher than that observed for free MeCN, and indicates an “end-on” coordination of MeCN to the Pd^{II} center [5*]. The ^1H NMR spectrum of **1** in $\text{MeNO}_2\text{-}d_3$ exhibited one singlet at 2.65 ppm indicating no exchange with the solvent. However, a solution of **1** in $\text{MeCN-}d_3$ showed only one absorbance at 1.98 ppm, corresponding to free MeCN. Thus all four MeCN ligands in **1** exchanged with the solvent immediately upon dissolution in $\text{MeCN-}d_3$ (eq. 5). The great lability of the MeCN ligands of **1** was



further indicated by their ready substitution by other ligands (Scheme 1).

The compounds, **2–5**, were synthesized through reactions analogous to eq. 3, as shown in eqs. 6, 7.

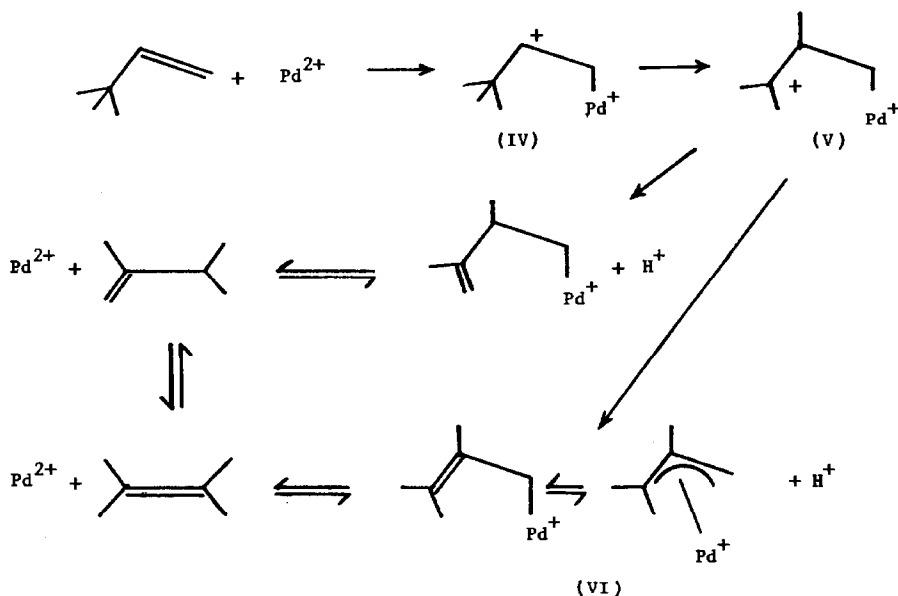


* Reference number with asterisk indicates a note in the list of references.

Table 2
Solvent dependence of the reactivity of the metal compounds, 1-5

Catalyst	Substrate	Substrate/ Catalyst	Solvent	Temperature (°C)	Time	Product	Yield (%)
$\text{Pd}(\text{CH}_3\text{CN})_4^{2+\text{a}}$	$\text{C}-\text{C}$	10	CH_3NO_2	25	20 min	$\text{C}=\text{C}$	90 ^f
$\text{Pd}(\text{CH}_3\text{CN})_4^{2+\text{a}}$	$\text{C}-\text{C}$	10	CH_3CN	25	20 min	$\text{C}=\text{C}$	90 ^f
$\text{Mo}(\text{NO})_2(\text{CH}_3\text{CN})_4^{2+\text{b}}$	$\text{C}-\text{C}$	10	CH_3NO_2	25	20 min	$\text{C}=\text{C}$	90 ^f
$\text{W}(\text{NO})_2(\text{CH}_3\text{CN})_4^{2+\text{b}}$	$\text{C}-\text{C}$	10	CH_3NO_2	25	20 min	$\text{C}=\text{C}$	90 ^f
$\text{W}(\text{NO})_2(\text{CH}_3\text{CN})_4^{2+\text{b}}$	$\text{C}-\text{C}$	10	CH_3CN	25	20 min	$\text{C}=\text{C}$	20
$\text{Co}(\text{CH}_3\text{CN})_6^{2+\text{c}}$	$\text{C}-\text{C}$	20	CH_3NO_2	25	2 days	$\text{C}=\text{C}$	40
$\text{Co}(\text{CH}_3\text{CN})_6^{2+\text{c}}$	$\text{C}-\text{C}$	20	CH_3CN	25	2 days	$\text{C}=\text{C}$	0
$\text{Ni}(\text{CH}_3\text{CN})_6^{2+\text{c}}$	$\text{C}-\text{C}$	20	CH_3NO_2	25	3 days	$\text{C}=\text{C}$	30
$\text{Ni}(\text{CH}_3\text{CN})_6^{2+\text{c}}$	$\text{C}-\text{C}$	10	CH_3CN	25	3 days	$\text{C}=\text{C}$	0
$\text{Pd}(\text{CH}_3\text{CN})_4^{2+\text{d}}$	$\text{PhCH}=\text{CH}_2$	100	CH_3NO_2	25	5 min	$((\text{Ph})\text{CHCH}_2)_n$	95
$\text{Pd}(\text{CH}_3\text{CN})_4^{2+\text{d}}$	$\text{PhCH}=\text{CH}_2$	100	CH_3CN	25	5 min	$((\text{Ph})\text{CHCH}_2)_n$	95
$\text{Mo}(\text{NO})_2(\text{CH}_3\text{CN})_4^{2+\text{e}}$	$\text{PhCH}=\text{CH}_2$	250	CH_3NO_2	25	4 h	$((\text{Ph})\text{CHCH}_2)_n$	95
$\text{W}(\text{NO})_2(\text{CH}_3\text{CN})_4^{2+\text{e}}$	$\text{PhCH}=\text{CH}_2$	250	CH_3NO_2	25	4 h	$((\text{Ph})\text{CHCH}_2)_n$	85
$\text{W}(\text{NO})_2(\text{CH}_3\text{CN})_4^{2+\text{e}}$	$\text{PhCH}=\text{CH}_2$	250	CH_3CN	25	4 h	$((\text{Ph})\text{CHCH}_2)_n$	0
$\text{Co}(\text{CH}_3\text{CN})_6^{2+\text{c}}$	$\text{PhCH}=\text{CH}_2$	100	CH_3NO_2	25	2 d	$((\text{Ph})\text{CHCH}_2)_n$	75
$\text{Co}(\text{CH}_3\text{CN})_6^{2+\text{c}}$	$\text{PhCH}=\text{CH}_2$	100	CH_3CN	25	2 d	$((\text{Ph})\text{CHCH}_2)_n$	0
$\text{Ni}(\text{CH}_3\text{CN})_6^{2+\text{c}}$	$\text{PhCH}=\text{CH}_2$	100	CH_3NO_2	25	3 d	$((\text{Ph})\text{CHCH}_2)_n$	40
$\text{Ni}(\text{CH}_3\text{CN})_6^{2+\text{c}}$	$\text{PhCH}=\text{CH}_2$	100	CH_3CN	25	3 d	$((\text{Ph})\text{CHCH}_2)_n$	0

^a [] = 9×10^{-2} M. ^b [] = 8.6×10^{-2} M. ^c [] = 5×10^{-2} M. ^d [] = 1.1×10^{-2} M. ^e [] = 1.7×10^{-1} M. ^f At equilibrium, the ratio of 2,3-dimethyl-2-butene to 2,3-dimethyl-1-butene $\sim 90/10$.

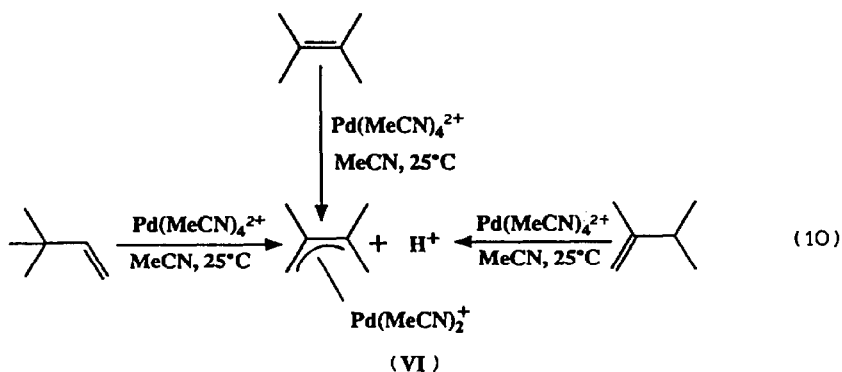


Scheme 2. Mechanism for the skeletal rearrangement of t-butylethylene by $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$.

C=C bond, as postulated by Hoffmann [14] for reactions involving nucleophilic attack on coordinated olefins. The species IV would then be expected to rearrange to the more stable tertiary carbocation, V, which would eventually lead to the observed products. The Pd compound that was formed in the course of the catalytic skeletal rearrangement is the η^3 -allyl compound, VI. In fact, this compound could be generated by adding either tert-butylethylene, 2,3-dimethyl-2-butene or 2,3-dimethyl-1-butene to a solution of 1 in MeCN (eq. 10).

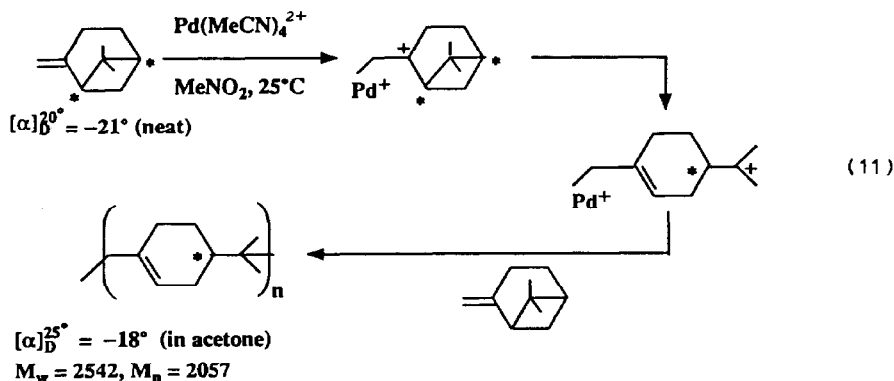
It is significant that the compounds, $\text{Pd}(\text{MeCN})_2\text{Cl}_2$ and $\text{Pd}(\text{MeCN})_{4-n}(\text{PPh}_3)_n^{2+}$ ($n = 2, 3$), which are expected to be weaker electrophiles than 1 did not catalyze the above skeletal rearrangement. The compounds 4 and 5 were also found to mediate the skeletal rearrangement but only in MeNO_2 and only in low yields. It is possible that the rate of skeletal rearrangement was a function of the relative freedom of the carbocation formed initially (e.g. species IV, Scheme 2). Reactions that proceed via carbocationic mechanisms do not necessarily require the same degree of carbocationic character in the intermediates involved. Thus it has been proposed [15] that in the acid catalyzed isomerization of 2-methylpent-2-ene, the methyl group migration requires more carbocationic character in the intermediate than does C=C bond migration. In our own work [2a,d,16,17], we have consistently observed that, for a given electrophilic metal center, the catalysis of C=C bond isomerization proceeded more readily than skeletal rearrangements.

The catalytic polymerization of 2(10)-pinene by 1 is another example of carbocation induced rearrangement [18*] (eq. 11). The polymer was formed within the time of mixing, and using a substrate/catalyst ratio of 100 and catalyst concentration of $1.1 \times 10^{-2} M$, a 97% isolated yield of the polymer was obtained. The C(1) and C(5) are the chiral centers in 2(10)-pinene. While the chirality is lost at C(1) during the polymerization, the mechanism as outlined in eq. 11, predicts complete retention at C(5), and indeed the polymer is optically active. While 2(10)-pinene has been



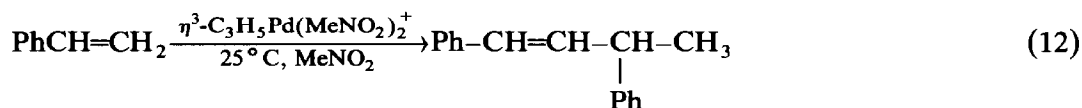
polymerized before [19], to our knowledge, there is no previous report of optical activity of the resultant polymer.

Electrophilic transition metal centers are expected to act as initiators for the cationic polymerization of olefins since carbocations are generated when they interact with olefins. The results of our studies on the polymerization and oligomerization of olefinic substrates by **1** and **4** are summarized in Table 3. Scheme 3 depicts a mechanism for the polymerization and oligomerization of olefins by electrophilic transition metal centers. According to this mechanism, the chain length of the polymer would depend on the relative rates of chain propagation (step A) versus chain termination by loss of H^+ (step B or C). If the rate of propagation is slow due to steric constraints (e.g. in $Ph(Me)C=CH_2$), or if the rate of termination by loss of H^+ is fast due to the lack of groups capable of strongly stabilizing the carbocation (e.g. in simple olefins such as $RCH=CH_2$, $R = H$, alkyl), then only dimers and the lower oligomers will be obtained. Carbocations are strongly destabilized in olefins bearing electron-withdrawing substituents (e.g. $CH_2=CHCOOMe$ and $CH_2=CHCN$), and they do not undergo cationic oligomerization or polymerization [20*]. If the activation energy for chain termination is greater than that for chain propagation, then the molecular weight would be expected to increase as the reaction temperature is lowered, due to the greater stability of the carbocations at



lower temperatures [21*]. We found this to be true for the polymerization of $\text{Ph}(\text{Me})\text{C}=\text{CH}_2$ by either **1** or **4**. At 25°C , only a mixture of indans, formed by the head-to-tail dimerization and trimerization, were observed. A similar dimerization of $\text{Ph}_2\text{C}=\text{CH}_2$ was also observed at 25°C . A rational mechanism for the formation of indans is shown in Scheme 4. The head-to-tail linkages arise naturally due to the greater stability of the hydrocarbyl substituted tertiary carbocations, compared to primary carbocations.

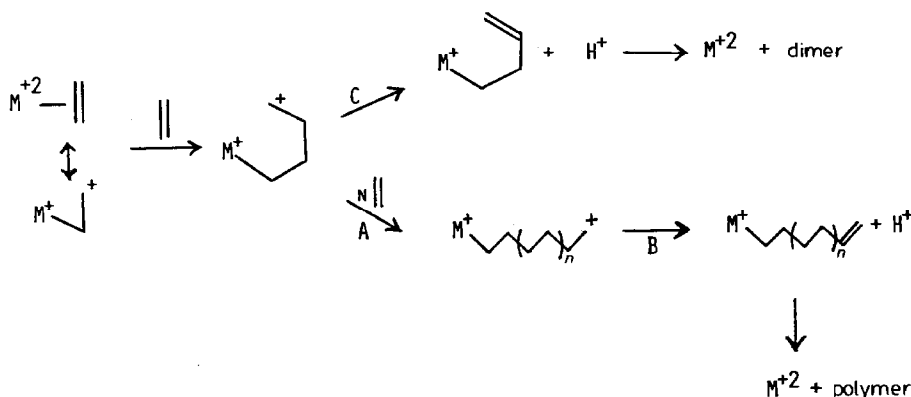
In order to determine the eventual fate of the catalyst in the olefin polymerization reactions, the following experiment was carried out. Following polymerization of $\text{PhCH}=\text{CH}_2$ by **1**, the Pd-containing species was recovered. Only broad resonances were observed in its ^1H NMR spectrum, thus preventing its proper characterization, but indicating that the Pd was attached to a polymeric residue. At 25°C , this species in MeNO_2 was found to catalyze the rapid conversion of $\text{PhCH}=\text{CH}_2$ to 1,3-diphenyl-1-butene rather than polystyrene! In a separate experiment, we found that the cationic η^3 -allyl complex, $[\eta^3\text{-C}_3\text{H}_5\text{Pd}(\text{MeNO}_2)_2](\text{BF}_4)$, was also a catalyst for the rapid dimerization of $\text{PhCH}=\text{CH}_2$ to 1,3-diphenyl-1-butene under identical conditions, (eq. 12) [22]. Thus, given the great tendency of **1** to react with olefins to produce cationic η^3 -allyl complexes (cf. eq. 10), it appears reasonable to postulate that the Pd species obtained following the catalytic polymerization of $\text{PhCH}=\text{CH}_2$ by **1** was also a cationic η^3 -allyl complex.



C. Reactions involving C–C bonds

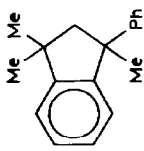
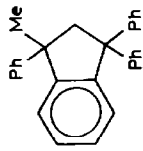

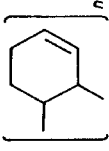
In the previous section, we have presented evidence for the heterolytic cleavage of the π -bond of olefins by electrophilic transition metal centers. A similar heterolytic





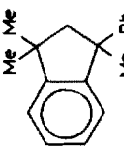
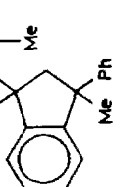
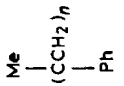
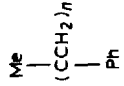
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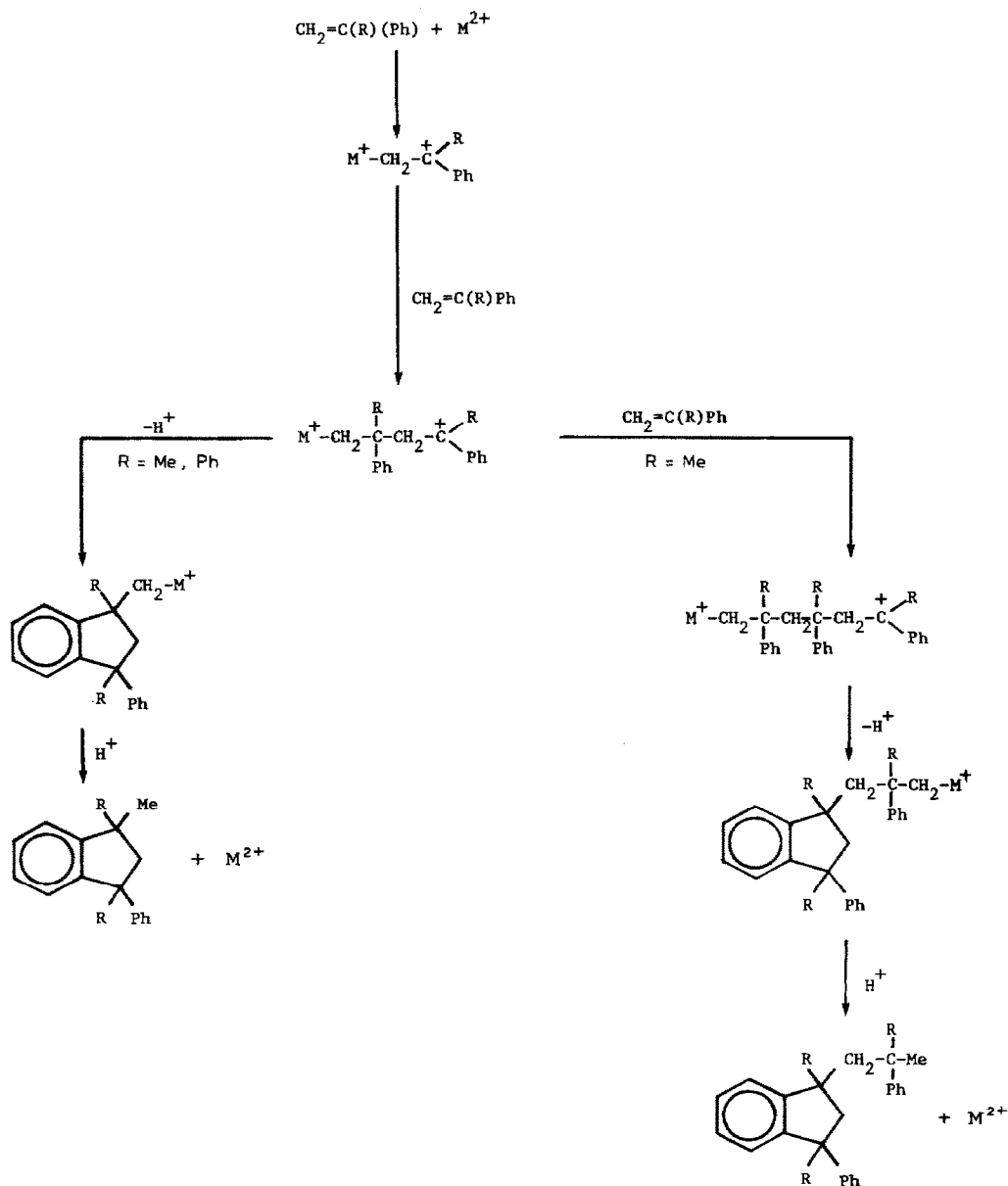
Scheme 3. Mechanism for the catalytic polymerization and oligomerization of olefins by electrophilic transition metal centers.

Table 3
 Polymerization and oligomerization of olefins catalysed by 1 and 4

Catalyst	Olefin	Olefin/ Catalyst	Solvent	Temperature (°C)	Time	Product	Yield (%)	Mol. Wt.
1 ^a	CH ₂ =CH ₂	- ^d	CH ₃ CN	25	1 h	(C ₂ H ₄) _n	- ^g	(n = 2-5) ^h
1 ^a	MeCH=CH ₂	- ^e	CH ₃ NO ₂	25	1 h	(C ₃ H ₆) _n	- ^g	(n = 2, 3) ^h
1 ^a	EtCH=CH ₂	- ^f	CH ₃ CN	25	1 d	(C ₄ H ₈) _n	- ^g	(n = 2) ^h
1 ^a	PhCH=CH ₂	100	CH ₃ CN	25	5 min	(CHCH ₂) _n Ph	95	70000 ⁱ
1 ^a	Ph(Me)C=CH ₂	100	CH ₃ NO ₂	25	10 h		80	-
1 ^a	Ph(Me)C=CH ₂	100	CH ₃ NO ₂	0	1 h	Me (CCH ₂) _n Ph	75	8000 ⁱ
1 ^a	Ph ₂ C=CH ₂	50	CH ₃ NO ₂	25	2 d		86	-
1 ^a	EtOCH=CH ₂	100	CH ₃ NO ₂	25	2 h	(CHCH ₂) _n OEt	95	insoluble
1 ^a		100	CH ₃ CN	25	30 min		40	2.000

1 ^a		100	CH ₃ NO ₂	25	5 min		96	insoluble
1 ^a		100	CH ₃ NO ₂	25	1 h		87	insoluble
4 ^b	Ph(Me)C=CH ₂	100	CH ₃ NO ₂	25	1 h	 + 	95	—
4 ^c	Ph(Me)C=CH ₂	200	CH ₃ NO ₂	0	6 h		95	8500 ⁱ
4 ^c	Ph(Me)C=CH ₂	200	CH ₃ NO ₂	-23	6 h		85	36000 ⁱ
1 ^a	CH ₂ =CHCOOMe	100	CH ₃ NO ₂	25	1 d	no reaction	—	—
1 ^a	CH ₂ =CHCN	100	CH ₃ NO ₂	25	1 d	no reaction	—	—

^a [] = 1.1 × 10⁻² M. ^b [] = 6.5 × 10⁻² M. ^c [] = 1.7 × 10⁻¹ M. ^d C₂H₄ pressure 1000 psi. ^e C₃H₆ pressure 120 psi. ^f C₄H₈ pressure 20 psi. ^g The yields could not be quantified due to high volatility. ^h Determined by GC-MS techniques. ⁱ Determined by GPC. The weights reported are those of the corresponding standard polystyrene samples.



Scheme 4. Mechanism for the catalytic conversion of substituted styrenes to indans by electrophilic transition metal centers.

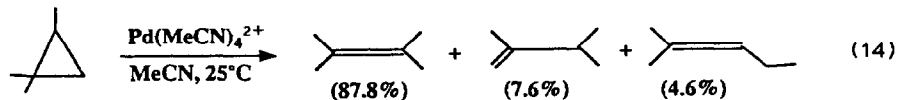
cleavage of C-C σ -bonds should also be possible (eq. 13), and indeed such a step



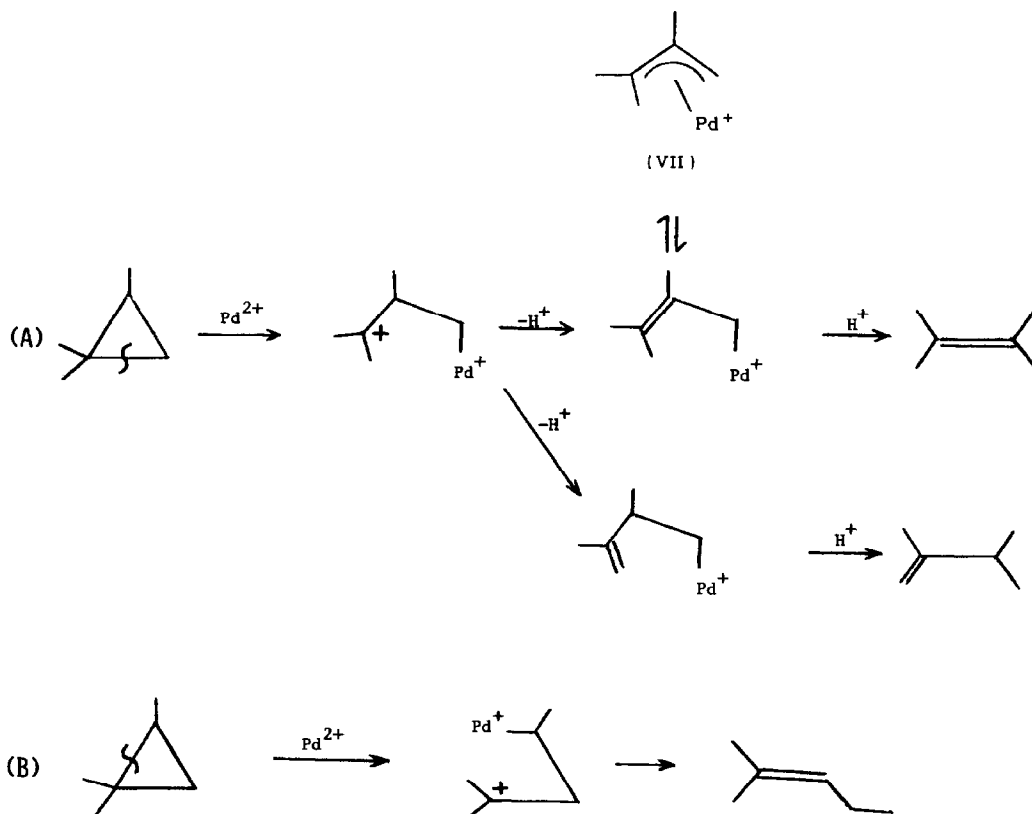
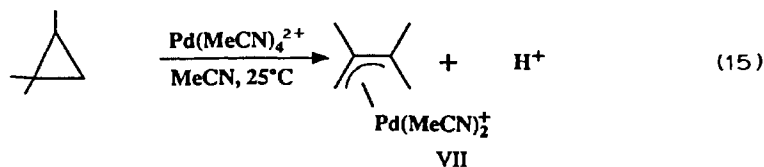
has been postulated by Halpern for several Ag^+ catalyzed rearrangements [23*]. More recently, results from theoretical studies of cyclopropane ring opening by Pd^{II} complexes indicated [24] that, as expected, this reaction pathway was favored by the

species, PdCl^+ , while high activation barriers were found for the less electrophilic species, PdCl_2 and PdCl_4^{2-} . With Pd^0 compounds, the favored pathway involved the oxidative addition of a C–C bond of the cyclopropane ring.

Three examples of catalytic rearrangement of the strained cyclopropane skeleton by **1** are cited in Table 4. A plausible mechanism for the rearrangement of 1,1,3-trimethylcyclopropane (eq. 14) is shown in Scheme 5. Paths A and B are the


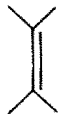
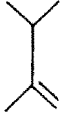
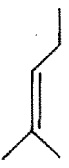
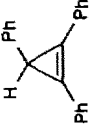
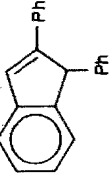




only cleavage modes that lead to the formation of the stable tertiary carbocation. Path A was presumably favored over path B due to steric reasons. The organometallic species observed in the course of the reaction is the cationic η^3 -allyl complex VII (eq. 15).

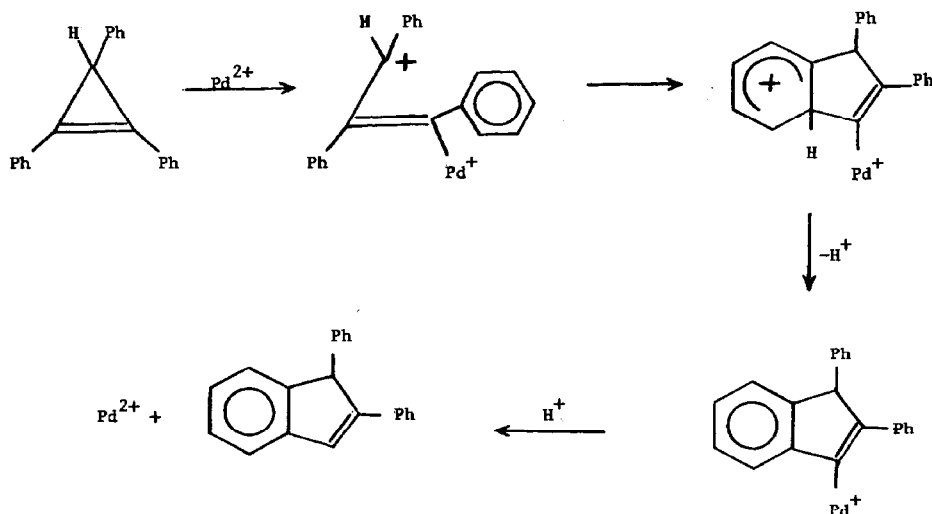


Scheme 5. Mechanism for the skeletal rearrangement of 1,1,2-trimethylcyclopropane by $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$.

Table 4
Catalytic rearrangements of the cyclopropane skeleton by **1**

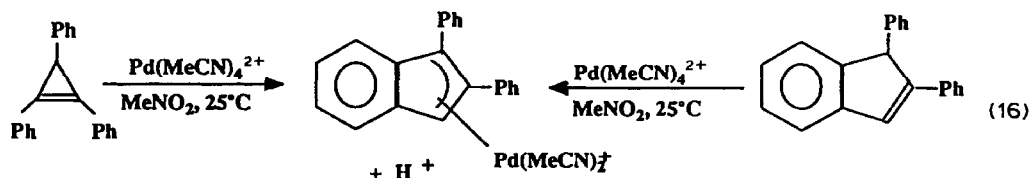
Catalyst	Substrate	Substrate/ catalyst	Solvent	Temperature (°C)	Time	Product	Yield (%)
1^a		20	CH ₃ NO ₂	25	6 h	 (87.8%)  (7.6%)  (4.6%)	100
1^a		10	CH ₃ NO ₂ -CHCl ₃	25	10 h		90
1^a		100	CH ₃ NO ₂	25	16 h	 (m.w. = 812) ^b	90

^a [] = 1.1×10^{-2} M. ^b Determined by osmometry in CHCl₃.

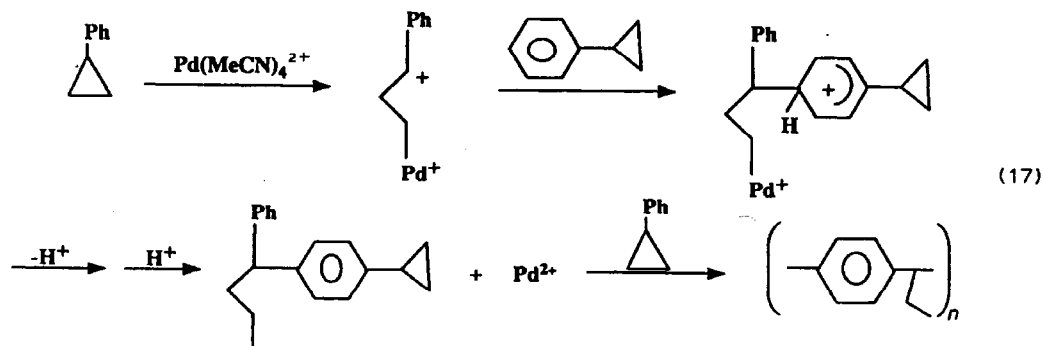


Scheme 6. Mechanism for the skeletal rearrangement of 1,2,3-triphenylcyclopropane by $[\text{Pd}(\text{CH}_3\text{CN})_4]$ $(\text{BF}_4)_2$.

A mechanistic pathway for the formation of 2,3-diphenylindene [25] is outlined in Scheme 6. A cationic η^3 -allyl Pd^{II} compound was also formed in this reaction (eq. 16).



Finally, a remarkable step-growth polymerization that is based on the electrophilic opening of cyclopropanes is the polymerization of cyclopropylbenzene that was catalyzed by **1**. The polymerization is initiated by the heterolytic C–C bond cleavage of the cyclopropane ring followed by the alkylation of the phenyl group of a second monomer by the resultant cation, the whole process then being repeated (eq. 17). Although the mechanism, as outlined, indicates a *para* substitution pattern for the phenyl group, both *ortho* and *para* substitutions are expected and were observed.



Experimental

Analytical instrumentation. IR spectra were recorded on a Perkin–Elmer Model 580 spectrophotometer. ^1H NMR spectra were recorded on either a Varian EM360 spectrometer or on Bruker WM360 and WP200 FT-NMR spectrometers. ^{13}C NMR spectra were recorded on Bruker WM360 and WP200 FT-NMR spectrometers. ^{31}P NMR spectra were recorded on a JEOL PS-100 FT-NMR spectrometer. UV-Vis spectra were recorded on a Hewlett–Packard Model 8450A spectrophotometer. Gas chromatography was performed on a Varian 3700 gas chromatograph equipped with a flame ionization detector. GC-MS data were obtained on a Finnigan 3200 computerized GC-MS equipment. The molecular weights of polymers were obtained by either osmometry (performed by Schwarzkopf Microanalytical Laboratory, New York) or gel permeation chromatography using equipment by Waters Associates. In the latter case, standard polystyrene samples were used for calibration. Elemental analysis was performed by Schwarzkopf Microanalytical Laboratory, New York.

General procedure. Reagent grade solvents were used. CHCl_3 , CH_2Cl_2 and MeCN were dried by distilling from CaH_2 followed by storage over P_2O_5 . C_6H_6 and Et_2O were dried by distilling from CaH_2 followed by storage over Na/benzophenone. MeNO_2 was dried by fractionally distilling from anhydrous CaCl_2 followed by storage over 4 Å molecular sieves. All solvents and liquid chemicals were deoxygenated by either vacuum distillation or by purging with N_2 prior to their use. All reactions were carried out either under vacuum or in a N_2 atmosphere. The transition metal compounds were stored in a N_2 filled dry box prior to use.

Preparation of $[\text{Pd}(\text{MeCN})_4](\text{BF}_4)_2$ (1) Method A [4]. 1.0 g of Pd sponge and 2.2 g of NOBF_4 were stirred in 50 ml of MeCN under vacuum. NO generated in the course of the reaction was removed periodically. After stirring for 12 h, the mixture was filtered to yield a yellow filtrate from which a pale yellow compound was obtained by the addition of anhydrous Et_2O . The compound was washed with anhydrous Et_2O and dried under vacuum (4.1 g, 98%). ^1H NMR (CD_3NO_2): 2.65(s). IR (Nujol): $\bar{\nu}(\text{C}\equiv\text{N})$, 2335, 2315 (vw) cm^{-1} ; $\bar{\nu}(\text{BF}_4^-)$, 1100–1000, 760 cm^{-1} . Anal. Found: C, 21.8; H, 2.9; N, 12.3. $\text{Pd}(\text{MeCN})_4(\text{BF}_4)_2$ calc.: C, 21.7; H, 2.7; N, 12.6%.

Method B. 0.5 g of PdCl_2 and 1.1 g of AgBF_4 were stirred in 40 ml of MeCN. A yellow solution and a white precipitate were formed. After stirring for 30 min, the mixture was filtered and the filtrate concentrated under reduced pressure. Addition of anhydrous Et_2O resulted in the precipitation of a yellow compound. This was collected and recrystallized from MeCN/ Et_2O . (1.19 g, 95%).

Preparation of $[\text{M}(\text{MeCN})_6](\text{BF}_4)_2$ ($\text{M} = \text{Ni}$, 2; Co , 3) [7]. A procedure analogous to that used for 1 in method A was followed.

Preparation of $[\text{M}(\text{NO})_2(\text{MeCN})_4](\text{BF}_4)_2$ ($\text{M} = \text{Mo}$, 4; W , 5). In a typical reaction, 1.5 g of $\text{W}(\text{CO})_6$ and 1.0 g of NOBF_4 were stirred in 35 ml of MeCN under vacuum. After stirring for 12 h, the mixture was filtered and the emerald green filtrate concentrated to 15 ml. Addition of 20 ml of anhydrous Et_2O resulted in the precipitation of a dark green solid. This was collected by filtration, washed with CH_2Cl_2 and dried under vacuum (1.96 g, 80%). IR (Nujol): $\bar{\nu}(\text{C}\equiv\text{N})$, 2330, 2300 cm^{-1} ; $\bar{\nu}(\text{NO})$, 1860, 1820, 1770, 1730 cm^{-1} ; $\bar{\nu}(\text{BF}_4^-)$, 1200–1000 cm^{-1} . Conductivity (MeCN): Slope ($\Delta_0 - \Delta_e$ vs. $\text{C}^{1/2}$) = 355. Anal. Found: C, 16.7; H, 2.1. $\text{W}(\text{NO})_2(\text{MeCN})_4(\text{BF}_4)_2$ calc.: C, 16.4; H, 2.1%.

$[\text{Mo}(\text{NO})_2(\text{MeCN})_4](\text{BF}_4)_2$ was prepared by an analogous procedure. IR (Nujol): $\bar{\nu}(\text{C}\equiv\text{N})$, 2360, 2310 cm^{-1} ; $\bar{\nu}(\text{NO})$, 1860, 1760, 1730 cm^{-1} ; $\bar{\nu}(\text{BF}_4^-)$, 1200–1000 cm^{-1} . Anal. Found: C, 19.0; H, 2.4. $\text{Mo}(\text{NO})_2(\text{MeCN})_4(\text{BF}_4)_2$ calc.: C, 19.5; H, 2.5%.

Preparation of $[\text{PdL}_4](\text{BF}_4)_2$, ($L = \text{PhCN}, \text{Me}_3\text{CCN}, \text{Py}$). These were typically prepared by the addition of an excess of the desired ligand to a solution of **1** in MeNO_2 . After stirring for 1 h under a N_2 atmosphere, the resultant solution was concentrated under vacuum. Addition of anhydrous Et_2O resulted in the precipitation of the desired Pd^{II} compound. This was washed with Et_2O and dried under vacuum. The absence of MeCN in these compounds was verified by ^1H NMR spectroscopy. $[\text{Pd}(\text{Me}_3\text{CCN})_4](\text{BF}_4)_2$. ^1H NMR (CD_3NO_2): 1.36(s). IR (Nujol): $\bar{\nu}(\text{C}\equiv\text{N})$, 2320 cm^{-1} . $[\text{Pd}(\text{PhCN})_4](\text{BF}_4)_2$. ^1H NMR (CD_3NO_2): 7.62 (m). IR (Nujol): $\bar{\nu}(\text{C}\equiv\text{N})$, 2300 cm^{-1} . $[\text{Pd}(\text{Py})_4](\text{BF}_4)_2$. ^1H NMR (CD_3NO_2): coordinated pyridine, 9.0, 8.1–7.8; free pyridine, 8.6, 7.8–7.3

Preparation of $[\text{Pd}(\text{MeCN})_x(\text{CO})_y](\text{BF}_4)_2$. CO was bubbled through a solution of **1** in MeCN at 25 °C for 1 h. The reaction mixture was then concentrated under vacuum. Following addition of Et_2O , an orange solid was obtained. This solid was unstable at 25 °C and decomposed within 6 h under a N_2 atmosphere. IR (Nujol): $\bar{\nu}(\text{C}\equiv\text{N})$, 2322 cm^{-1} ; $\bar{\nu}(\text{CO})$, 2120 cm^{-1} .

Preparation of $[\text{Pd}(\text{MeCN})_{4-n}(\text{PPh}_3)_n](\text{BF}_4)_2$, ($n = 2, 3$). In a typical reaction, 0.25 g of **1** and 0.295 g of PPh_3 (2 equiv. relative to **1**) were stirred in 30 ml of CH_2Cl_2 for 1 h. Following concentration of the yellow solution under vacuum, a yellow solid was obtained by adding anhydrous Et_2O . The compound was washed with Et_2O and dried under vacuum (0.40 g, 80%). ^1H NMR (CD_3NO_2): 7.4–7.2 (30 H, m); 1.85 (6 H, s), ^{31}P NMR $\{^1\text{H}\}(\text{CDCl}_3, -50^\circ\text{C})$: 32.1(s) ppm. IR (Nujol): $\bar{\nu}(\text{C}\equiv\text{N})$, 2335 cm^{-1} ; $\bar{\nu}(\text{BF}_4^-)$, 1100–1000 cm^{-1} . $[\text{Pd}(\text{MeCN})(\text{PPh}_3)_3](\text{BF}_4)_2$ was synthesized in an analogous reaction, starting with 0.2 g of **1** and 1.2 g of Ph_3P (0.48 g, 97%). ^{31}P NMR $\{^1\text{H}\}(\text{CDCl}_3, -40^\circ\text{C})$: 34.5 ppm (1P, t, $J(\text{PP})$ 11.7 Hz); 27.6 ppm (2P, d, $J(\text{PP})$ 11.7 Hz). IR (Nujol): $\bar{\nu}(\text{C}\equiv\text{N})$, 2335 cm^{-1} ; $\bar{\nu}(\text{BF}_4^-)$, 1100–1000 cm^{-1} .

*Reaction with tetrakis(*p*-anisyl)ethylene, (TAE).* In a typical reaction, a solution of 25 mg of **1** in 2 ml of MeCN was added to a solution of 100 mg of TAE [9] in 1 ml of CHCl_3 . An immediate blue coloration was observed. Attempts to isolate the TAE- Pd^{2+} adduct failed, presumably due to its instability.

The reactions of TAE with other metal compounds and Br_2 were carried out in an analogous manner.

*Catalytic skeletal rearrangement of *t*-butylethylene by **1**.* 0.22 g of **1** was dissolved in 50 ml of MeCN and 6.37 ml of *t*-butylethylene was added. The resulting reaction mixture was then stirred at 25 °C for 24 h, following which the organic products were separated from the Pd compounds formed by vacuum distillation. The organic products were analyzed by GC using a Porapak N column, and their identities confirmed by comparison with authentic samples and by GC-MS techniques. A 20% yield of 88/12 mixture of 2,3-dimethyl-2-butene and 2,3-dimethyl-1-butene was obtained, together with a small amount of $\text{C}_{12}\text{H}_{24}$ olefins.

The Pd compound formed in the reaction was $[\eta^3\text{-}(\text{CH}_2\text{CMeCMe}_2)\text{Pd}(\text{MeCN})_2](\text{BF}_4)$. ^1H NMR (CD_3CN): 3.95 (1H, broad s); 3.36 (1H, broad s); 2.1 (3H, s); 1.5 (3H, s); 1.3 (3H, s); 1.98 (6H, s, MeCN). IR (MeCN): $\bar{\nu}(\text{C}\equiv\text{N})$, 2335 cm^{-1} ; $\bar{\nu}(\text{BF}_4^-)$, 1100–1000 cm^{-1} . This compound was also formed by the reaction of

either 2,3-dimethyl-2-butene or 2,3-dimethyl-1-butene with **1** in MeCN at 25 °C.

Catalytic polymerization of 2(10)-pinene by 1. (–)-2(10)-pinene (1.8 ml) was added to a solution of **1** (50 mg) in MeNO₂ (10 ml) and the resulting mixture stirred at 25 °C for 1 h. A cloudy yellow solution was formed and this was poured in 50 ml of CHCl₃ and then eluted through a short stem silica gel column. Following this procedure, the solvent was removed, and the solid obtained was dried at 50 °C under vacuum (1.5 g, 97%). ¹H NMR (CDCl₃): 5.3, 1.9, 1.6, 0.9 (all broad). IR (KBr): 2950, 2920, 2810, 1460, 1430, 1385, 1365 cm⁻¹. The ¹H NMR spectrum was found to match with that reported previously [26].

Catalytic oligomerization of C₂H₄, C₃H₆ and C₄H₈ by 1. 50 mg of **1** dissolved in 10 ml of MeCN was placed in a Parr bomb and pressurized with C₂H₄ to 1000 psi. After stirring at 25 °C for 1 h, the gases were vented and the organic products separated from the catalyst by vacuum distillation. Analysis of the organic products by GC using a Porapak N column indicated the formation of C₄H₈, C₆H₁₂ and C₈H₁₆, together with a smaller amount of C₁₀H₂₀. This was confirmed by GC-MS techniques. The composition of the C₄H₈ isomers was 6% 1-butene, 67% *trans*-2-butene and 28% *cis*-2-butene.

A similar procedure was used for C₃H₆ (at 120 psi) and C₄H₈ (at 20 psi).

Catalytic polymerization of PhCH=CH₂. 1.3 ml of PhCH=CH₂ was added to a solution of **1** (50 mg) in MeCN (10 ml). After stirring at 25 °C for 5 min, the viscous reaction mixture was added to 100 ml of CHCl₃. The resulting yellow solution was then eluted through a silica gel column. Following evaporation of the solvent and drying of the solid at 50 °C under vacuum, a white solid was obtained. (1.12 g, 95%). ¹H-NMR (CDCl₃): 7.06 (3H, broad); 6.6 (2H, broad); 2.4–1.1 (3H, broad). IR (KBr): 3150, 1600, 1580, 1500, 1450, 758, 695 cm⁻¹.

Similar procedure was used in reactions where **2**, **3**, **4** or **5** were used as catalysts.

In the reactions where the Pd compound was recycled, the following procedure was used. 2.6 ml of PhCH=CH₂ was added to a solution of **1** (0.1 g) in MeNO₂ (30 ml). The resulting mixture was vigorously stirred at 25 °C for 10 min. The viscous solution formed was filtered to remove polystyrene, yielding a yellow-orange filtrate. This solution slowly turned orange on standing under N₂ for 1 h. To this solution was added 2.6 ml of PhCH=CH₂. After stirring at 25 °C for 6 h, a ¹H NMR spectrum indicated the quantitative formation of 1,3-diphenyl-1-butene. The solution was then eluted through a silica gel column. Following evaporation of the solvent and drying, a clear liquid was obtained. See below for spectral parameters.

Catalytic dimerization of PhCH=CH₂ by [η³-C₃H₆Pd(MeNO₂)₂](BF₄). 0.1 g of (η³-C₃H₅PdCl)₂ [27] and 0.11 g of AgBF₄ were stirred in 20 ml of CH₃NO₂ and 10 ml of CHCl₃ at 25 °C for 30 min. The resulting mixture was then filtered to remove AgCl, yielding a yellow filtrate. To this solution was added 2.8 g of PhCH=CH₂. After stirring at 25 °C for 1 day, the solution was eluted through a silica gel column. Following evaporation of the solvent a clear liquid was obtained (2.6 g, 94%). ¹H-NMR (CDCl₃): 7.4–7.2 (10H, m); 6.38 (2H, d, 5 Hz); 3.63 (1H, m, 5 Hz, 6.9 Hz); 1.45 (3H, d, 6.9 Hz). ¹³C-NMR {¹H}(CDCl₃): 145.5, 137.5, 135.1, 128.6–126.1, 42.5, 21.2. Mol. wt. (CHCl₃): found, 212; calc., 208. Hydrogenation product: 1,3-diphenylbutane. ¹H NMR (CDCl₃): 7.3–7.1 (10 H, m); 2.65 (1H, m, 7 Hz, 7 Hz); 2.50 (2H, t, 7.6 Hz); 1.90 (2H, m, 7 Hz, 7.6 Hz); 1.24 (3H, d, 7 Hz).

Catalytic oligomerization of Ph(Me)C=CH₂ at 25 °C. In a typical reaction, 32 mg of **4** was dissolved in 1 ml of MeNO₂, and to this solution 0.84 ml of

$\text{Ph}(\text{Me})\text{C}=\text{CH}_2$ was added slowly with stirring. After stirring for 1 h, a viscous solution was obtained. This was added to 30 ml of CHCl_3 and then eluted through a short stem silica gel column to remove the catalyst. An oil was obtained after evaporation of the solvent. (0.75 g, 95%). The product consisted of two major products as shown by TLC. Flash chromatography using 0.2 g of the mixture and 100 ml of hexane separated the two fractions. 1-Phenyl-1,3,3-trimethylindan and 1-phenyl-3-(2-phenyl-2-methylpropyl)-1,3-dimethylindan were obtained in the ratio of 1/3.

1-Phenyl-1,3,3-trimethylindan. ^1H NMR (CDCl_3): 7.4–7.0 (9H, m); 2.45, 2.18 (2H, ABq, 12.8 Hz); 1.69 (3H, s); 1.32 (3H, s); 1.03 (3H, s). ^{13}C NMR $\{^1\text{H}\}(\text{CDCl}_3)$: 150.9–148.7, 127.9–122.5, 59.4, 50.8, 42.8, 30.8, 30.4. Mass spec. (m/e): 236, (M^+), 221, ($M^+ - \text{CH}_3$).

1-Phenyl-3-(2-phenyl-2-methylpropyl)-1,3-dimethylindan. ^1H NMR (CDCl_3): 7.4–7.0 (14H, m); 2.59, 1.92 (2H, ABq, 13.4 Hz); 2.16, 1.70 (2H, ABq, 14.6 Hz); 1.61 (3H, s); 1.28 (3H, s); 1.14 (3H, s); 0.95 (3H, s). ^{13}C NMR $\{^1\text{H}\}(\text{CDCl}_3)$: 153.7–148.3, 127.9–122.9, 57.4, 54.9, 51.2, 47.6, 38.6, 33.4, 30.8, 29.2, 28.6. Mass spec. (m/e): 339, ($M^+ - \text{CH}_3$).

A similar procedure was used when **1** was used as a catalyst. 1-Phenyl-1,3,3-trimethylindan was the only major product (> 90%) observed.

Catalytic polymerization of $\text{Ph}(\text{Me})\text{C}=\text{CH}_2$ at low temperatures. In a typical reaction, **4** (86 mg) was dissolved in MeNO_2 (1 ml) and the solution was cooled to 0°C . 5.0 ml of $\text{Ph}(\text{Me})\text{C}=\text{CH}_2$ was added, and then the reaction mixture stirred at 0°C for 6 h. At the end of this period, 30 ml of CHCl_3 was added and the resulting mixture eluted through a short stem silica gel column to remove the catalyst. Removal of the solvent under vacuum gave a white polymer (4.47 g, 98%). ^1H NMR (CDCl_3): 7 (5H, broad); 1.5 (2H, broad); 0.1 (3H, broad). IR (KBr): 3080, 3050, 3020, 2980, 2922, 1595, 1575, 1445, 1380, 760, 700 cm^{-1} . The ^1H NMR spectrum compared well with that reported earlier [28].

A similar procedure was used at -23°C or when **1** was used as a catalyst.

*Catalytic dimerization of $\text{Ph}_2\text{C}=\text{CH}_2$ by **1**.* 0.4 ml of $\text{Ph}_2\text{C}=\text{CH}_2$ was added to a solution of **1** (50 mg) in MeNO_2 (10 ml). The reaction mixture was stirred at 25°C for 2 days. 50 ml of CHCl_3 was then added and the resulting mixture was eluted through a short stem silica gel column to remove the Pd compound. After removing the solvent and drying the solid under vacuum, 1,3,3-triphenyl-3-methylindan was obtained (0.35 g, 86%).

^1H NMR (CDCl_3): 7.4–7.0 (19H, m); 3.45, 3.10 (2H, ABq, 12 Hz); 1.6 (3H, s). ^{13}C NMR $\{^1\text{H}\}(\text{CDCl}_3)$: 150.5–147.5, 128.8–125.0, 61.4, 60.9, 51.2, 28.9. Mass spec. (m/e): 360, (M^+); 283 ($M^+ - \text{C}_6\text{H}_5$).

*Catalytic polymerization of $\text{EtOCH}=\text{CH}_2$ by **1**.* 1 ml of $\text{EtOCH}=\text{CH}_2$ was added to a solution of **1** (50 mg) in MeNO_2 (10 ml), and the reaction mixture was stirred at 25°C for 12 h. At the end of this period, the white precipitate formed was collected, washed with MeCN and CHCl_3 , and dried at 50°C under vacuum (0.6 g, 75%). The poly(vinyl ethyl ether) was insoluble in CHCl_3 , CH_2Cl_2 and CH_3CN . IR (KBr): 2975, 2925, 2875, 1370, $1150\text{--}1050\text{ cm}^{-1}$. The IR spectrum was consistent with those of related polyvinyl ethers [29].

*Catalytic polymerization of 1,3-cyclohexadiene by **1**.* 1.1 ml of 1,3-cyclohexadiene was added to a solution of **1** (50 mg) in MeCN (10 ml). The reaction mixture was stirred at 25°C for 30 min. The resulting yellow viscous solution was then added to

CHCl_3 (50 ml) and eluted through a short stem silica gel column to remove the catalyst. The solvent was then removed under vacuum to yield a white polymer (0.35 g, 40%). The ^1H NMR spectrum of poly(1,3-cyclohexadiene) and its structural implications were discussed in ref. 2b,c.

Catalytic polymerization of norbornene by 1. Norbornene (1.0 g) and **1** (50 mg) were together stirred in MeNO_2 at 25°C for 5 min. The reaction mixture solidified during stirring. The white solid was repeatedly washed with MeNO_2 and then dried under vacuum at 50°C (0.96 g, 95%). The poly(norbornene) was insoluble in CHCl_3 , CH_2Cl_2 and C_6H_6 . IR (KBr): 2940, 2870, 1475, 1295 cm^{-1} . The IR spectrum and its structural implications were discussed in ref. 2b,c.

Catalytic polymerization of norbornadiene by 1. 1.04 g of norbornadiene was added to a solution of **1** (50 mg) in MeNO_2 (10 ml). After stirring at 25°C for 1 h, the solution became viscous. The solvent was removed under vacuum and the resulting solid was washed repeatedly with MeCN. Finally, the solid was dried at 50°C under vacuum (0.9 g, 87%). The polymer was insoluble in CHCl_3 , CH_2Cl_2 and C_6H_6 . The IR spectrum of poly(norbornadiene) and its structural implications were discussed in ref. 2b,c.

Catalytic ring opening of 1,1,2-trimethylcyclopropane by 1. To a solution of **1** (50 mg) in MeNO_2 (10 ml) was added 0.185 g of 1,1,2-trimethylcyclopropane. After stirring for 6 h at 25°C , the organic products were separated from the Pd compound formed by vacuum distillation. The products were analyzed by GC using a 20% AgNO_3 in ethylene glycol on Chromosorb. The identity of the compounds was verified by comparison with authentic samples. The Pd compound isolated from the reaction mixture was $[\eta^3\text{-(CH}_2\text{CMe}_2\text{)Pd(MeCN)}_2\text{]BF}_4$.

Catalytic ring opening of 1,2,3-triphenylcyclopropene by 1. A CHCl_3 (5 ml) solution of 1,2,3-triphenylcyclopropene (0.3 g) was added to a solution of **1** (50 mg) in MeNO_2 (5 ml). The resulting mixture was stirred at 25°C for 10 h. At the end of this period, the reaction mixture was eluted through a short stem silica gel column to remove the catalyst. After evaporation of the solvent, 2,3-diphenyl-1-indene was obtained as the only organic product (0.27 g, 90%). ^1H NMR (CDCl_3): 7.3 (15H, m); 5.00 (1H, s). ^{13}C NMR $\{^1\text{H}\}$ (CDCl_3): 149.9, 149.1, 143.2, 140.0, 135.1, 128.9, 128.5, 128.0, 127.9, 127.3, 127.0, 126.7, 126.6, 125.5, 123.8, 121.1, 56.3. The ^1H NMR spectrum was identical with that reported earlier [30].

The formation of the cationic η^3 -allyl complex in the above reaction (eq. 16) was verified as follows. A mixture of a 0.5 ml CD_3NO_2 solution of **1** (50 mg) and a 0.5 ml CDCl_3 solution of 1,2,3-triphenylcyclopropene (40 mg) was stirred at 25°C for 1.5 h. At the end of this period, a ^1H NMR spectrum of the resulting solution indicated the presence of the η^3 -allyl complex together with 2,3-diphenyl-1-indene and unreacted 1,2,3-triphenylcyclopropene. ^1H NMR ($\text{CD}_3\text{NO}_2/\text{CDCl}_3$): 7.5–7.2, 6.4, 2.15 (coordinated MeCN). See ref. 25 for a previous report concerning an analogous η^3 -allyl complex of Pd^{II} .

The same η^3 -allyl complex was also formed starting with 2,3-diphenyl-1-indene, as shown by the following experiment. A 0.5 ml CD_3NO_2 solution of **1** (50 mg) was added to a 0.5 ml CDCl_3 solution of 2,3-diphenyl-1-indene (30 mg, 1 equiv. relative to **1**). 23 mg of anhydrous Na_2CO_3 was then added and the reaction mixture stirred for 4 h at 25°C . At the end of this period, the reaction mixture was filtered to yield a dark red solution. The ^1H NMR spectrum of this solution indicated a 60% conversion of 2,3-diphenyl-1-indene to the η^3 -allyl complex.

Catalytic polymerization of phenylcyclopropane by 1. 1.38 ml of phenylcyclopropane and 50 mg of **1** were stirred together in 10 ml of MeNO₂ at 25 °C for 16 h. At the end of this period, 100 ml of CHCl₃ was added and the resulting mixture was eluted through a short stem silica gel column to remove the catalyst. After removing the solvent and drying under vacuum, a white polymer was obtained. ¹H NMR (CDCl₃): 7.17 (4H, broad); 3.63 (1H, broad); 1.96 (2H, broad); 0.84 (3H, broad). ¹³C NMR {¹H}(CDCl₃): 145.3, 142.7, 128.8, 128.3, 127.8, 125.9, 52.9, 52.5, 28.9, 28.7, 12.8. Selected ¹³C NMR (¹H-coupled) data: 52.9 (d, 125 Hz, CH); 52.5 (d, 125 Hz, CH); 28.9 (t, 125 Hz, CH₂); 28.7 (t, 125 Hz, CH₂); 12.8 (q, 125 Hz, CH₃). Both *ortho*- and *para*-linkages are present in the polymer, and this causes small differences in ¹³C NMR chemical shifts for the corresponding CH and CH₂ groups.

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