a-c plane, owing to the occurrence of diagonal contacts associated with (+[+]+) environments; the relatively low probability and random distribution of these branching interactions within the two-dimensional networks, however, suggest that they are properly regarded as defects within predominantly one-dimensional magnetic chains along a. Physical studies on solid solutions of the type $[[TMTSF]_2Ni(tds)_2]_x[Cu(tds)_2]_{1-x}$ should provide further information about the magnetic properties of these compounds.

Acknowledgment. This work was supported by the Solid State Chemistry Program of the National Science Foundation (Grant DMR 85-19233 to B.M.H.) and by the Northwestern University Materials Research Center under the NSF-MRL program (DMR 85-20280). We further acknowledge Johnson Matthey Inc. for the loan of platinum salts.

Registry No. $[TMSF]_2[Ni(Tds)_2]$, 102784-07-6; $[TMSF]_2[Pt(tds)_2]$, 102764-53-4; $[TMSF]_2[Cu(tds)_2]$, 111557-31-4.

Supplementary Material Available: Tables of positional and anisotropic thermal parameters (2 pages); listing of structure amplitudes for both the room- and low-temperature structures (20 pages). Ordering information is given on any current masthead page.

Mechanism of Acyl Group Isomerization in Palladium(II) Complexes. Development of a Catalytic Process for the Isomerization of Carboxylic Acid Chlorides

Jeffrey S. Brumbaugh and Ayusman Sen*[1]

Contribution from Chandlee Laboratory, Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802. *Received April 6, 1987*

Abstract: $[Pd(PPh_3)_2(MeCN)(CO^iPr)](BF_4)$ (**2c**), when dissolved in a variety of weakly coordinating polar solvents, spontaneously isomerized to an equilibrium mixture of **2c** and $[Pd(PPh_3)_2(MeCN)(CO^nPr)](BF_4)$ (**2d**). Several other complexes having the general formula $[Pd(PPh_3)_2(MeCN)(COR)](BF_4)$ also underwent spontaneous isomerization, including those involved in the following isomer systems: R = ^{n}Bu/^{s}Bu, ^{i}Bu/^{t}Bu, and methylcyclohexyl. In each system the more stable isomer was that having the least branching in the alkyl group. When R was a vinyl group, the complex decomposed to form the respective vinyltriphenylphosphonium salt. The reactions were first order in metal complex and inverse first order in MeCN. PPh_3 inhibited the reactions by promoting metal complex decomposition. When the isomerizations were carried out in the presence of an excess of ethylene or cyclohexene, $[Pd(PPh_3)_2(MeCN)(COEt)](BF_4)$ (**2b**) or $[Pd(PPh_3)_2(MeCN)(COC_6H_{11})](BF_4)$ (**2n**) respectively, was produced in high yields. Concomitant with the formation of **2b** in the reaction of $[Pd(PPh_3)_2(MeCN)(COC_7H_{13})](BF_4)$ with ethylene was the formation of methylenecyclohexane, 1-methylcyclohexene, 3-methylcyclohexene, and 4-methylcyclohexene. When the reaction was carried out in $CDCl_3$, a small quantity of $CHDCl_2$ was generated as a byproduct, arising from the reaction of an intermediate metal hydride with the solvent. A key intermediate in the reaction mechanism was postulated to be $[Pd(PPh_3)_2(H)(CO)(olefin)](BF_4)$, which was formed from the starting material via the following sequence of events: (a) MeCN dissociation, (b) CO deinsertion, and (c) β-hydrogen abstraction. The reversal of steps a-c generated the isomeric acyl compound. The corresponding neutral palladium-acyl complexes, $Pd(PPh_3)_2(Cl)(CO^iPr)$ and $Pd(PPh_3)_2(Cl)(CO^nPr)$, underwent isomerization to an equilibrium mixture of these isomers when a Lewis acid or $[Pd(PPh_3)_2(MeCN)(COR)](BF_4)$ was employed as a catalyst. Finally, the catalytic isomerization of isobutyryl chloride or n-butyryl chloride to an equilibrium mixture of these organic acids was promoted by either $[Pd(PPh_3)_2(MeCN)(COR)](BF_4)$ or a combination of $Pd(PPh_3)_2(Cl)(COR)$ and $AlCl_3$.

Transition-metal-acyl complexes are ubiquitous and those belonging to the later transition metals are actively involved in a large number of catalytic and stoichiometric carbonylation and decarbonylation reactions. These include the hydroformylation[2] and carbonylation[3] of olefins, the copolymerization of olefins with carbon monoxide,[4] the carbonylation of alcohols[5] and alkyl and aryl halides,[6] and the decarbonylation of aldehydes and carboxylic acid chlorides.[7] However, despite the central role played by metal-acyl complexes in these reactions, the question of their structural integrity has not been addressed in detail. The product regiospecificity in many of the above reactions will depend on the propensity toward acyl isomerization in the intermediate metal-acyl compounds (eq I).

$$M\text{-}COCHRCH_2R' \rightleftharpoons M\text{-}COCHR'CH_2R \qquad (I)$$

Prior to our work, the isomerization of the acyl group in $Co(CO)_4(COR)$[8] and $Rh(PPh_3)_2(CO)_2(COR)$[9] had been briefly reported; however, no mechanistic information was available concerning these systems. Herein, we report the results of our studies on the spontaneous acyl group isomerization in cationic palladium(II) complexes. These studies have also led to the development of a novel palladium-catalyzed process for the

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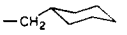
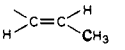
(2) Reviews: (a) Cornils, B. In *New Syntheses with Carbon Monoxide*; Falbe, J., Ed.; Springer-Verlag: Berlin, 1980; p 1. (b) Pruett, R. L. *Adv. Organomet. Chem.* **1979**, *17*, 1. (c) Marko, L. In *Aspects of Homogeneous Catalysis*; Ugo, R., Ed.; Reidel: Dordrecht, 1974; Vol. 2, p 3.
(3) Review: Mullen, A. In ref 2a; p 243.
(4) (a) Sen, A. *Adv. Polym. Sci.* **1986**, *73/74*, 125. (b) Lai, T.-W.; Sen, A. *Organometallics* **1984**, *3*, 866. (c) Sen, A.; Lai, T.-W. *J. Am. Chem. Soc.* **1982**, *104*, 3520.
(5) (a) Dekleva, T. W.; Forster, D. *J. Am. Chem. Soc.* **1985**, *107*, 3565, 3568. Reviews: (b) Bahrmann, H.; Cornils, B. In ref 2a; p 226. (c) Drury, D. J. In ref 2c, 1984; Vol. 5, p 197.
(6) Reviews: (a) Heck, R. F. *Adv. Catal.* **1977**, *26*, 323. (b) Weil, T. A.; Cassar, L.; Foa, M. In *Organic Syntheses via Metal Carbonyls*; Wender, I., Pino, P., Eds.; Wiley: New York, 1972; Vol. 2, p 517. Leading references for the related "double carbonylation" of halides: (c) Ozawa, F.; Soyama, H.; Yanagihara, H.; Aoyama, I.; Takino, H.; Izawa, K.; Yamamoto, T.; Yamamoto, A. *J. Am. Chem. Soc.* **1985**, *107*, 3235. (d) Chen, J.-T.; Sen, A. *J. Am. Chem. Soc.* **1984**, *106*, 1506.
(7) Review: Tsuji, J.; Ohno, K. *Synthesis* **1969**, 157.
(8) (a) Ungvary, F.; Marko, L. *Organometallics* **1982**, *1*, 1120. (b) Masada, H.; Mizuno, M.; Suga, S.; Watanabe, Y.; Takegami, Y. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 3824. (c) Takegami, Y.; Watanabe, Y.; Masada, H.; Okuda, Y.; Kubo, K.; Kokokawa, C. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 1495. (d) Takegami, Y.; Yokokawa, C.; Watanabe, Y. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 2430. (e) Takegami, Y.; Yokokawa, C.; Watanabe, Y.; Masada, H.; Okuda, Y. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 787. (f) Takegami, Y.; Yokokawa, C.; Watanabe, Y.; Okuda, Y. *Bull. Chem. Soc. Jpn.* **1964**, *37*, 181. (g) Takegami, Y.; Yokokawa, C.; Watanabe, Y.; Masada, H.; Okuda, Y. *Bull. Chem. Soc. Jpn.* **1964**, *37*, 1190. (h) Rupilius, W.; Orchin, M. *J. Org. Chem.* **1972**, *37*, 936.
(9) Brown, J. M.; Kent, A. G. *J. Chem. Soc., Chem. Commun.* **1982**, 723.

0002-7863/88/1510-0803$01.50/0

Table I. Physical and Spectral Properties for Complexes of the General Formula $Pd(PPh_3)_2(Cl)(COR)$

A

	R	% yield[a]	color	IR ($\bar{\nu}_{CO}$)[b]	^{31}P NMR[c]		R	% yield[a]	color	IR ($\bar{\nu}_{CO}$)[b]	^{31}P NMR[c]
1a	Me	95	white	1688	18.65	**1i**		85	white	1686	18.66
1b	Et	97	white	1685	18.76						
1c	*i*-Pr	94	white	1662 1692	19.01	**1j**		79	pl. yel.	1665	16.46
1c* [d]	*i*-Pr	81	white		17.21	**1k**	-CMe=CH_2	97	pl. yel.	1642 1629	19.26
1d	*n*-Pr	91	white	1688	18.83						
1e	*sec*-Bu	81	pl. yel.	1688	19.05	**1l**		98	pl. yel.	1616	19.66
1f	*n*-Bu	93	white	1678 1669	18.77	**1m**	-CH=CMe_2	97	yellow	1647	18.45
1g	*t*-Bu	98	pl. yel.	1682 1654	16.92	**1n**		94	white	1670	19.10
1h	*i*-Bu	86	white	1681	18.90	**1o**	Ph	93	pl. yel.	1638	18.83
						1o* [d]	Ph	94	pl. yel.	1665	17.03

B

complex	^1H NMR data[c,e]	complex	^1H NMR data[c,e]
1a	1.40 (s, 3 H), 7.38 (m, 18 H), 7.72 (m, 12 H)	**1i**	0.01 (br m, 2 H), 0.28 (br s, 1 H), 0.76 (br m, 5 H), 1.25 (br m, 3 H), 2.12 (d, J = 6 Hz, 2 H), 7.40 (m, 18 H), 7.72 (m, 12 H)
1b	−0.32 (t, J = 7 Hz, 3 H), 1.98 (q, J = 7 Hz, 2 H), 7.41 (m, 18 H), 7.77 (m, 12 H)	**1j**	0.62–1.74 (br m, 13 H), 7.11 (m, 18 H), 8.10 (m, 12 H)
1c	0.62 (d, J = 7 Hz, 6 H), 1.55 (m, J = 7 Hz, 1 H), 7.38 (m, 18 H), 7.75 (m, 12 H)	**1k**	0.67 (s, 3 H), 5.67 (s, 1 H), 6.88 (s, 1 H), 7.37 (m, 18 H), 7.76 (m, 12 H)
1c* [d]	0.75 (d, J = 7 Hz, 6 H), 1.58 (m, J = 7 Hz, 1 H), 2.25 (s, 18 H), 7.1 (m, 12 H), 7.5 (m, 12 H)	**1l**	1.31 (d, J = 6.6 Hz, 3 H), 4.78 (d, J = 15.4 Hz, 1 H), 6.72 (dq, J = 15.4, 6.6 Hz, 1 H), 7.41 (m, 18 H), 7.79 (m, 12 H)
1d	0.12 (t, J = 7 Hz, 3 H), 0.35 (m, J = 7 Hz, 2 H), 1.92 (t, J = 7 Hz, 2 H), 7.38 (m, 18 H), 7.75 (m, 12 H)	**1m**	1.16 (br s, 6 H). 5.82 (br s, 1 H), 7.37 (m, 18 H), 7.77 (m, 12 H)
1e	0.33 (m, J = 7 Hz, 2 H), 0.37 (t, J = 7 Hz, 3 H), 0.64 (d, J = 7 Hz, 3 H), 1.70 (m, J = 7 Hz, 1 H), 7.32 (m, 18 H), 7.67 (m, 12 H)	**1n**	0.21 (br m, 2 H), 0.55 (br m, 3 H), 1.24 (br m, 4 H), 1.88 (d, J = 12.7 Hz, 2 H), 7.32 (m, 18 H), 7.68 (m, 12 H)
1f	0.43 (m, J = 7 Hz, 2 H), 1.94 (t, J = 7 Hz, 3 H), 7.35 (m, 18 H), 7.70 (m, 12 H)	**1o**	7.2–7.8 (m)
1g	0.61 (s, 9 H), 7.38 (m, 18 H), 7.74 (m, 12 H)	**1o*** [d]	2.29 (s, 18 H), 7.0 (m, 15 H), 7.5 (m, 14 H)
1h	0.03 (d, J = 6 Hz, 6 H), 0.60 (m, J = 6 Hz, 1 H), 2.17 (d, J = 6 Hz, 2 H), 7.36 (m, 18 H), 7.66 (m, 12 H)		

C

complex	^{13}C NMR data[c,e]	complex	^{13}C NMR data[c,e]
1b	7.1 (q, $^1J_{C-H}$ = 129 Hz), 48.2 (tt, $^1J_{C-H}$ = 126 Hz, $^3J_{P-C}$ = 14 Hz), 126.6–136.9 (m, phenyl carbons), 237.1 (s)	**1g**	27.5 (q, $^1J_{C-H}$ = 127 Hz), 54.4 (t, $^3J_{P-C}$ = 15 Hz), 126.6–136.7 (m, phenyl carbons), 239.4 (s)
1c	17.9 (q, $^1J_{C-H}$ = 127 Hz), 50.4 (dt, $^1J_{C-H}$ = 125 Hz, $^3J_{P-C}$ = 17 Hz), 126.1–137.1 (m, phenyl carbons), 239.8 (s)	**2h**	1.4[f] (q, $^1J_{C-H}$ = 138 Hz), 21.9 (br q, $^1J_{C-H}$ = 126 Hz), 25.5 (br d, $^1J_{C-H}$ = 129 Hz), 62.8 (br t, $^1J_{C-H}$ = 130 Hz), 124.5[f] (t, $^3J_{P-C}$ = 10 Hz), 127.4–135.6 (m, phenyl carbons), 224.4 (s)

[a] Isolated. [b] Nujol mull (cm^{-1}). [c] $CDCl_3$ (ppm). [d] $(p\text{-}CH_3C_6H_4)_3P$ derivative. [e] Multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. [f] Coordinated CH_3CN.

isomerization of carboxylic acid chlorides.[10] The latter allows the first experimental determination of the relative free energies of formation for isomeric acid chlorides and, by extrapolation, other isomeric alkyl derivatives.

Results

A. Synthesis of Palladium(II)–Acyl Complexes. *trans*-$Pd(PPh_3)_2(Cl)(COR)$ derivatives were prepared by the oxidative addition of the corresponding carboxylic acid chlorides to $Pd(PPh_3)_4$ (eq 1). Pale yellow or white solids were isolated and were characterized by spectroscopic methods (Table I).

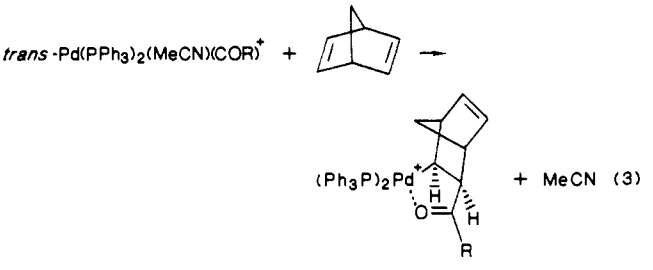
$$Pd(PPh_3)_4 + RCOCl \rightarrow \textit{trans}\text{-}Pd(PPh_3)_2(Cl)(COR) \quad (1)$$

The cationic Pd(II)–acyl compounds were synthesized by the metathesis of the corresponding neutral complexes with $AgBF_4$ in the presence of MeCN (eq 2). Because of their propensity

$$\textit{trans}\text{-}Pd(PPh_3)_2(Cl)(COR) \xrightarrow[MeCN\text{-}CH_2Cl_2]{AgBF_4} \textit{trans}\text{-}Pd(PPh_3)_2(MeCN)(COR)^+BF_4^- \quad (2)$$

toward isomerization in solution, special techniques were employed in the isolation of the compounds (see Experimental Section). The cationic complexes were soluble in polar solvents ($CHCl_3$, CH_2Cl_2, MeCN, $MeNO_2$, $PhNO_2$, DMSO) but not in the less polar ethers and hydrocarbons. All complexes adopt the trans square-planar configuration and their spectroscopic data are given in Table II.

B. Analysis of Palladium(II)–Acyl Functionality. In addition to ^1H and ^{31}P NMR spectroscopy, two other techniques were employed to detect and characterize the cationic Pd(II)–acyl species that were present in solution. The first involved the insertion of norbornadiene into the Pd–COR bond of $Pd(PPh_3)_2(COR)(MeCN)^+$, a reaction that proceeded quantitatively and rapidly (<20 min under experimental conditions) in accordance



with eq 3.[11] The inserted product was easily identified by a characteristic pair of doublets centered at ~35 and 12 ppm (J_{P-P} = 42 Hz) in the ^{31}P NMR spectrum. Reaction 3 proved valuable

(10) A previous attempt at the catalytic isomerization of acyl chlorides did not lead to thermodynamic mixtures and was accompanied by side products, see: Foglia, T. A.; Barr, P. A.; Idacavage, M. J. *J. Org. Chem.* **1976**, *41*, 3452.

(11) Brumbaugh, J. S.; Whittle, R. R.; Parvez, M. A.; Sen, A., manuscript in preparation.

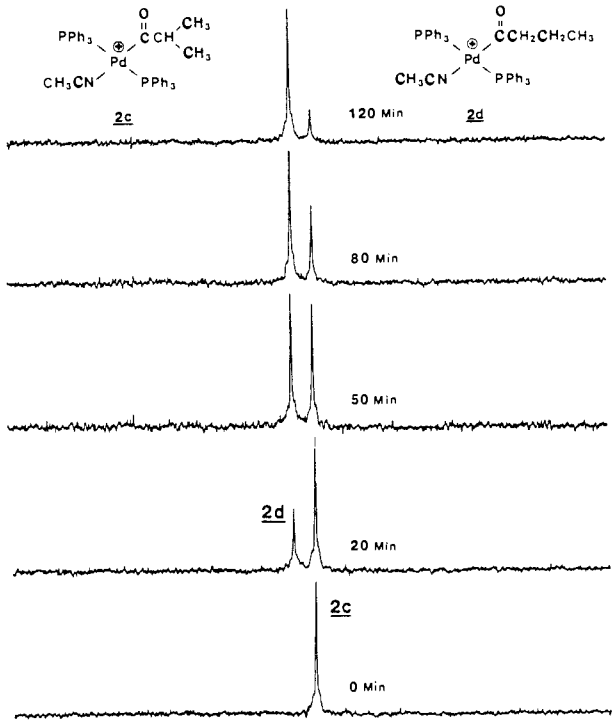
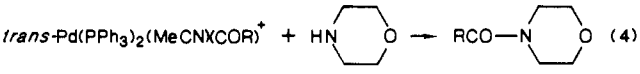


Figure 1. Isomerization of **2c** to **2d** as observed by ^{31}P NMR spectroscopy.

in analyzing ^{31}P NMR resonances with regard to whether the particular signals present were due to Pd(II)–acyl cations or some other P-containing species.

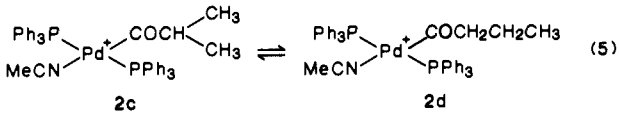
A second technique involved the reaction of the cationic Pd(II)–acyls with morpholine to quantitatively generate the corresponding amides (eq 4). This reaction proceeded virtually in-



stantaneously and could be used to quench the isomerization process at any desired time for kinetic studies. The amides were readily analyzed qualitatively and quantitatively by GC and GC–MS techniques.

C. Isomerization of Cationic Palladium(II) Acyls. For simplicity, the isomeric acyls will be designated according to their respective alkyl (rather than acyl) groups. For example, the equilibrium between **2c** and **2d** will be referred to as the ^{i}Pr–^{n}Pr equilibrium. The advantage of this nomenclature becomes more apparent as the acyl groups increase in complexity.

2c was observed to isomerize to an equilibrium mixture (K_{eq} = 5.1 ± 0.3) of **2c** and **2d** in $CDCl_3$ at 25 °C (eq 5). When monitored by ^{31}P NMR spectroscopy, a singlet at 19.82 ppm due



to **2d** was found to grow in intensity at the expense of the singlet at 19.32 ppm due to **2c** (Figure 1). The new resonance continued to replace the old one until a limiting ratio of 5.1:1 was attained, after which time no further change in the ^{31}P NMR spectrum was observed. At no time during the isomerization was any resonance detected that could be attributed to an intermediate.

The addition of norbornadiene to the solution caused a change in the spectrum from a pair of singlets to two sets of doublet of doublets (Figure 2), thus confirming that the new product, like the reactant, was a Pd(II)–acyl cation. The logical assumption that the acyls were isomeric was verified by reaction with morpholine to produce a 5.1:1 mixture of *n*-butyrylmorpholine and isobutyrylmorpholine. In addition, the ^{1}H NMR spectrum of the solution was consistent with a 5.1:1 mixture of **2c** and **2d**. Finally, that the system had truly reached a dynamic equilibrium was

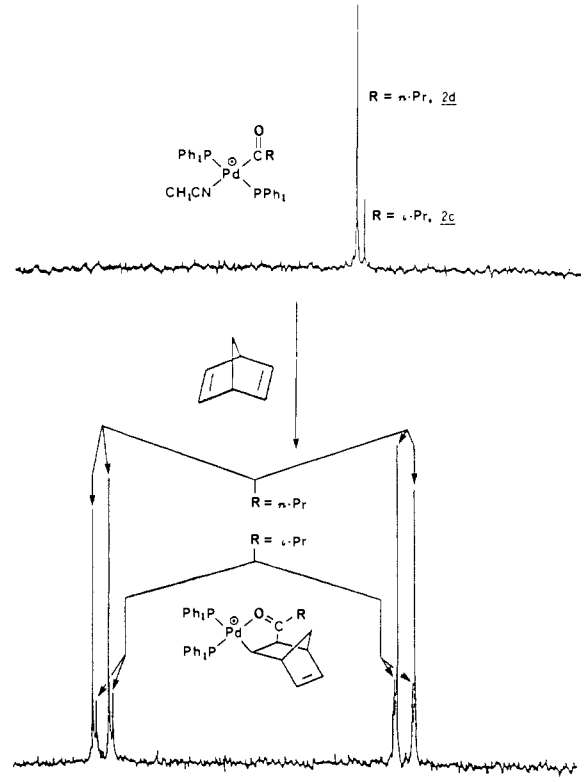


Figure 2. Addition of norbornadiene to the equilibrium mixture of **2c** and **2d** to form the respective olefin-inserted products as observed by ^{31}P NMR spectroscopy.

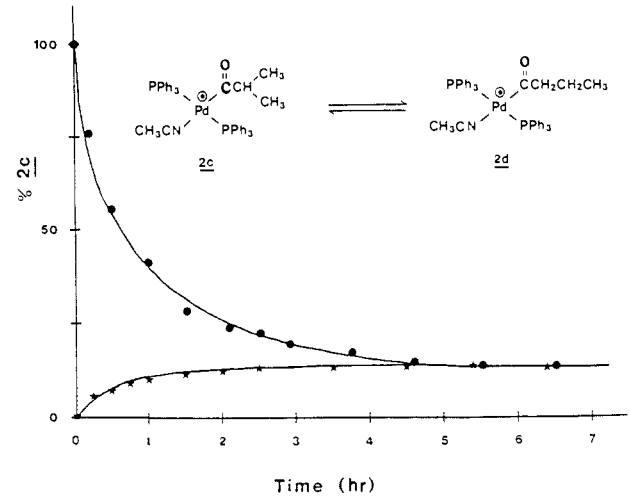


Figure 3. Plot of percent **2c** versus time indicating the attainment of a dynamic equilibrium.

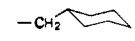
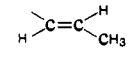
confirmed when **2d**, in $CDCl_3$ at 25 °C, generated the same product distribution as that starting with **2c**. Figure 3 shows a plot of percent **2c** with time when starting from either **2c** or **2d**.

The isomerization readily occurred in a variety of weakly coordinating solvents, such as $CHCl_3$, CH_2Cl_2, Me_2CO, $MeNO_2$, and $PhNO_2$. However, no isomerization was observed in MeCN after 1 week at 25 °C. This allowed the synthesis and the acquisition of spectral data of the pure compounds in solution.

During the course of the isomerization, the reaction solution remained pale yellow and homogeneous. Eventually, but well after the equilibrium had been reached, the color darkened to yellow-brown, and unidentified decomposition products (<10%) appeared in the ^{31}P NMR spectrum. When the reaction was carried out in $CDCl_3$, $CHDCl_2$ was detected by ^{1}H NMR spectroscopy. This was presumably formed by the reaction of an intermediate Pd(II)–H species with the solvent. The origin of the decomposition is discussed in the Kinetics section (section E).

Table II. Physical and Spectral Properties for Complexes of the General Formula $[Pd(PPh_3)_2(CH_3CN)(COR)](BF_4)$

A

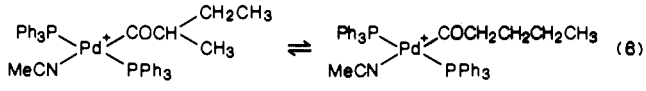
	R	% yield[a]	color	IR ($\bar{\nu}_{CO}$)[b]	IR ($\bar{\nu}_{CN}$)[b]	^{31}P NMR[c]
2a	Me	95	white	1693	2243 2272	19.4
2b	Et	97	white	1689	2245 2272	19.80
2c	*i*-Pr	94	white	1680 1701	2253 2280	19.32
2c* [d]	*i*-Pr	65	white			18.62
2d	*n*-Pr	85	white	1695	2265 2300	19.82
2e	*sec*-Bu	75	yellow	1695	2247 2275	19.40
2f	*n*-Bu	92	white	1703 1685	2240 2268	19.80
2g	*t*-Bu	87	yellow	1660 1693	2262 2295	17.64
2h	*i*-Bu	83	white	1714 1698	2268 2300	19.71
2i		92	white	1705	2242 2272	19.70
2j		83	off-white	1689	2248 2278	17.37
2k	-CMe=CH_2	87	tan	1668	2258 2282	20.29
2l		80	tan	1632 1641	2246 2272	20.38
2m	-CH=CMe_2	80	tan	1667	2245 2273	19.97
2n		75	white	1688	2238 2267	19.34
2o	Ph	93	white	1660	2240 2267	19.98
2o* [d]	Ph	88	pl. yel.	1658	2242 2270	18.30

B

complex	^1H NMR data[e,f]	complex	^1H NMR data[e,f]
2a[c]	1.42 (s, 3 H), 1.50 (t, $^3J_{P-H}$ = 1.6 Hz, 3 H), 7.56 (m, 30 H)	**2i**	0.03 (br m, 2 H), 0.41 (br m, 1 H), 0.76 (br m, 5 H), 1.24 (br m, 3 H), 2.16 (d, *J* = 6.6 Hz, 2 H), 7.56 (m, 30 H)
2b[c]	0.10 (t, *J* = 7 Hz, 3 H), 1.50 (br s, 3 H), 2.05 (q, *J* = 7 Hz, 2 H), 7.55 (m, 30 H)	**2j**	0.55 (s, 3 H), 0.88–1.37 (m, 10 H), 7.52 (m, 30 H)
2c	0.64 (d, *J* = 7 Hz, 6 H), 1.65 (m, *J* = 7 Hz, 1 H), 7.57 (m, 30 H)	**2k**	0.90 (s, 3 H), 5.85 (s, 1 H), 6.67 (s, 1 H), 7.58 (m, 30 H)
2c* [d]	0.68 (d, *J* = 7 Hz, 6 H), 1.72 (m, *J* = 7 Hz, 1 H), 2.30 (s, 18 H), 7.11 (m, 12 H), 7.32 (m, 12 H)	**2l**	1.29 (dd, *J* = 6.6, 1.5 Hz, 3 H), 4.86 (dd, *J* = 15.4, 1.5 Hz, 1 H), 6.82 (dq, *J* = 15.4, 6.6 Hz, 1 H), 7.62 (m, 30 H)
2d	0.12 (t, *J* = 7 Hz, 3 H), 0.50 (m, *J* = 7 Hz, 2 H), 2.00 (t, *J* = 7 Hz, 2 H), 7.56 (m, 30 H)	**2m**	1.16 (d, *J* = 1 Hz, 3 H), 1.21 (d, *J* = 1 Hz, 3 H), 5.94 (m, 1 H), 7.52 (m, 30 H)
2e	0.44 (br m, 5 H), 0.70 (d, *J* = 7 Hz, 3 H), 1.95 (m, 1 H), 7.55 (m, 30 H)	**2n**[c]	0.22 (br m, 2 H), 0.49 (br m, 3 H), 1.25 (br m, 4 H), 1.34 (s, 3 H), 7.46 (m, 30 H)
2f	0.44 (m, 7 H), 2.03 (t, *J* = 7 Hz, 2 H), 7.56 (m, 30 H)	**2o**[c]	1.52 (s, 3 H), 7.0–7.7 (m, 35 H)
2g	0.66 (s, 9 H), 7.54 (m, 30 H)	**2o*** [d]	1.54 (s, 3 H), 2.33 (s, 18 H), 7.01 (t, *J* = 7 Hz, 2 H), 7.15 (d, *J* = 8 Hz, 13 H), 7.33 (m, 12 H), 7.46 (d, *J* = 7 Hz, 2 H)
2h	0.10 (d, *J* = 6 Hz, 6 H), 0.78 (m, 1 H), 2.20 (d, *J* = 6 Hz, 2 H), 7.56 (m, 30 H)		

[a] Isolated. [b] Nujol mull (cm^{-1}). [c] $CDCl_3$ (ppm). [d] $(p\text{-}CH_3C_6H_4)_3P$ derivative. [e] CD_3CN, unless otherwise noted (ppm). [f] Multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad.

Analogous to the propyl system discovered above, an equilibrium mixture was formed (in ~4 h) when either **2e** or **2f** was dissolved in $CDCl_3$ at 25 °C (eq 6). K_{eq} was calculated to be 10.7 ± 1.1

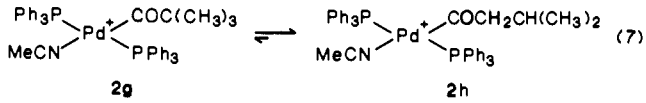


(6)

2e **2f**

from both ^{31}P NMR spectroscopy and gas chromatography (by integration of the corresponding amides formed by morpholine cleavage). Slow decomposition was again observed, but only after the system had reached equilibrium. At no time were any other butyl isomers (**2g** or **2h**) detected.

When monitored by ^{31}P NMR spectroscopy, **2g** was observed to convert to **2h** in $CDCl_3$ at 25 °C (eq 7). This reaction was, however, significantly slower than those discussed above, and after



(7)

2g **2h**

1 week the ratio of **2g** to **2h** had reached 1:10. By this time the solution color had changed from pale yellow to yellow-brown and deposits of Pd metal were observed. The ^{31}P NMR spectrum now contained, in addition to singlets from **2g** and **2h**, resonances at 22.8 and 36.1 ppm, suggesting partial system decomposition (~10% by integration). Also suggesting decomposition was the detection of isobutylene and free MeCN by ^1H NMR spectroscopy.

When **2h** was dissolved in $CDCl_3$ at 25 °C, formation of **2g** was detected by neither ^{31}P nor ^1H NMR spectroscopy even after 1 week. Decomposition was again evident, as both the resonances at 22.8 and 36.1 ppm were present in the ^{31}P NMR spectrum.

Although these results are apparently inconsistent with the dynamic equilibrium of eq 7, olefin substitution experiments (section D) indicate that the equilibrium does exist but cannot be reached when starting with **2g**, due to substantial product decomposition en route. The decomposition products, particularly MeCN, slow the reaction such that equilibrium is never reached. That no detectable amount of **2g** was formed from **2h** is presumably a result of the equilibrium thermodynamics greatly favoring **2h** over **2g**. Allowing for a minimum detection limit of 2% by ^{31}P NMR spectroscopy, a lower limit of 50 for K_{eq} was thus calculated.

The 1-methylcyclohexanoyl cation, **2j**, was found to isomerize to a mixture of (methylcyclohexyl)acyl isomers, when dissolved in $CDCl_3$ at 25 °C. The ^{31}P NMR resonance of **2j** at 17.37 ppm was initially replaced by two new singlets at 19.68 and 19.31 ppm. Over the next few days, other resonances between 19 and 20 ppm were observed to grow in and out. After 5 days, the system had apparently reached equilibrium, as no further change in the ^{31}P NMR spectrum was observed. Present at this time were singlets at 19.23, 19.33, and 19.70 ppm, integrating to a ratio of 45:35:20, respectively. Addition of norbornadiene to the mixture confirmed that the new products were Pd(II)–acyl cations, as all the singlets were quantitatively replaced by pairs of doublets, corresponding to their respective olefin-inserted products.

After 1 week in $CDCl_3$ at 25 °C, the isomeric cyclohexylacetyl cation, **2i**, isomerized to the same equilibrium mixture. This reaction primarily differed from the former in two aspects. First, at no time was the presence of any **2j** detected by ^{31}P NMR spectroscopy. Second, the resonance due to **2i** at 19.70 ppm was initially replaced by only one resonance at 19.31 ppm. As in the

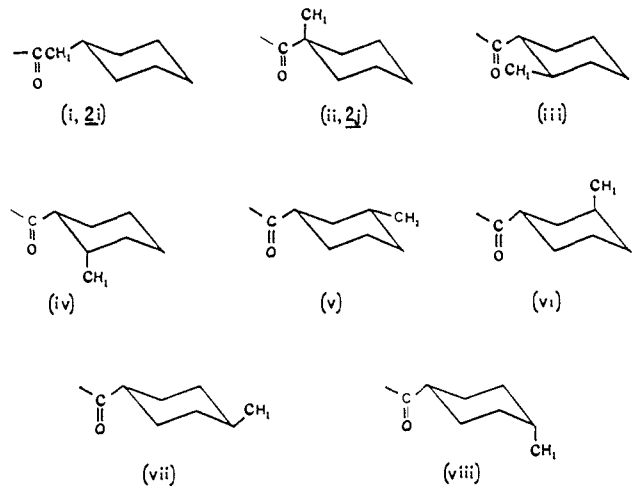


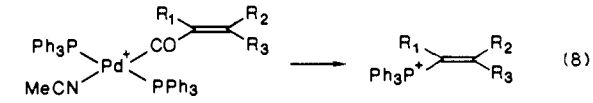
Figure 4. Eight possible (methylcyclohexyl)acyl isomers of the type, $Pd(PPh_3)_2(CH_3CN)(COR)^+$.

former reaction, many intermediate acyls were formed, only to subsequently disappear prior to the establishment of equilibrium. That both systems formed the same product distribution indicated that a dynamic equilibrium had been attained, despite the observation that significant decomposition occurred en route. Approximately 25% of the ^{31}P NMR signals at the end of both reactions were attributed to decomposition products. As in the ^tBu–^iBu systems, 95% of the decomposed products consisted of two unidentified resonances at 38.1 and 22.8 ppm. The remaining 5% was identified as $HPPh_3^+BF_4^-$. Consistent with the decomposition was a gradual color change of the reaction mixture from pale yellow to dark yellow-brown, with the simultaneous deposition of Pd metal.

Assuming the $L_3Pd(CO-)$ unit to be large and hence in the equatorial position, the eight (methylcyclohexyl)acyl isomers, i–viii (Figure 4), may in theory be present in a dynamic equilibrium. That only three isomers were detected by ^{31}P NMR spectroscopy is therefore a consequence of the high thermodynamic stabilities of these three relative to the others. Since the ^1H NMR spectrum of the original product mixture was not well resolved, the assignment of structures to the reaction products was based primarily on the ^1H NMR spectrum of the corresponding mixture of amides formed by morpholine cleavage. Three distinct resonances, corrsponding to protons α to a carbonyl group, were observed between 2.0 and 2.5 ppm. One, a doublet centered at 2.17 ppm (J = 6.6 Hz), was unambiguously assigned to isomer i. This assignment is consistent with the ^1H NMR data for **2i**. The remaining two resonances (2.37 and 2.47 ppm) were both triplets of triplets (J = 11.8 and 3.3 Hz for both). Isomers ii–iv would not exhibit such a splitting pattern and are thus eliminated, leaving behind only v–viii as possibilities. On the tentative assumption that v and vii would be the more stable isomers, both having only equatorial substituents on the cyclohexyl ring, the remaining two resonances were assigned to these isomers. Furthermore, the more predominant of the two species was probably vii, since its methyl group is both equatorial and farthest away from the bulky Pd moiety.

Thus, the equilibrium mixture consisted of the acyl isomers, i, vii, and v, in the ratio 45:35:20. It should be noted, however, that two other products were detected in small concentrations (<5%) by gas chromatography of the amides. Any attempt to assign structures to these isomers would be purely speculative.

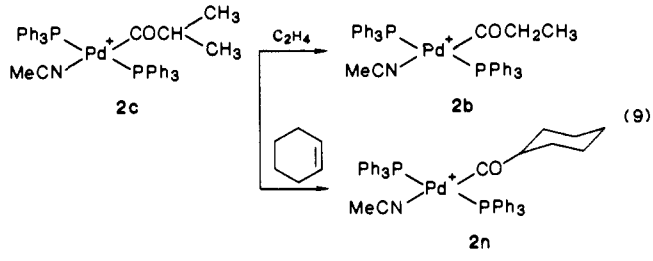
To explore the generality of the acyl isomerization reaction, compounds containing vinylacyl ligands were synthesized and their reactivities were examined. No isomerization was observed when the compounds **2k–m** were dissolved in $CDCl_3$. Instead, these complexes decomposed to form the corresponding vinyl phosphonium salts (eq 8).[12] The same result was also obtained in



(**2k**: R_1 = Me, R_2 = R_3 = H; **2l**: R_1 = R_3 = H, R_2 = Me; **2m**: R_1 = H, R_2 = R_3 = Me)

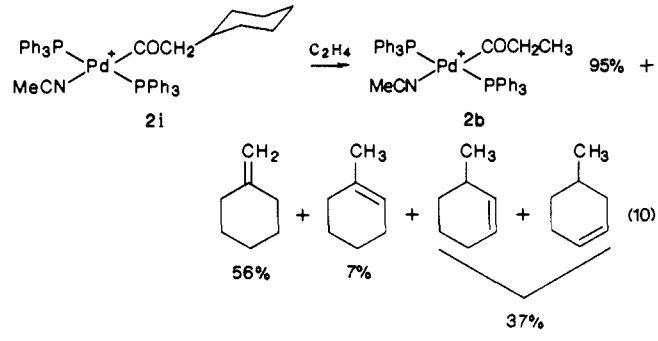
CD_2Cl_2, CD_3NO_2, and $C_6D_5NO_2$. However, in analogy with the isomerization reactions described above, no decomposition was observed in CD_3CN at 25 °C, even after 1 week.

D. Olefin Exchange Reactions. In addition to the expected isomeric products, products derived from olefin substitution were observed when the isomerizations were carried out in $CDCl_3$ in the presence of an excess of added olefin. For example, **2c**, in C_2H_4-saturated $CDCl_3$ at 25 °C, formed *trans*-$Pd(PPh_3)_2(MeCN)(COEt)^+BF_4^-$ (**2b**), in 90% yield in 1 h (eq 9). Similarly, **2c**, in a 0.7 M solution of cyclohexene in $CDCl_3$ at 25 °C, formed the corresponding cyclohexylacyl cation, **2n**, in 44% yield in 16 h (eq 9). The formation of **2b** and **2n** by the reaction of **2c** with

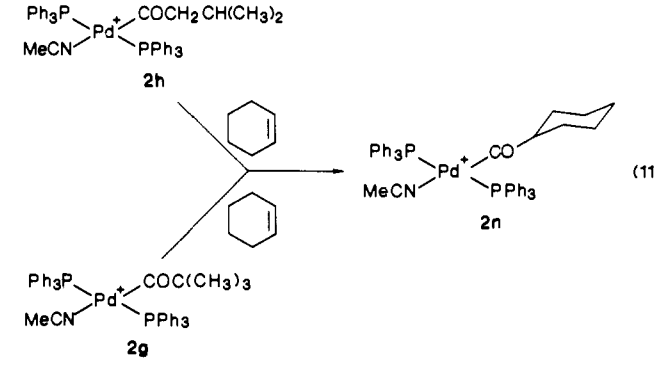


C_2H_4 and C_6H_{10}, respectively, implies the existence of a reaction intermediate containing a labile olefin. That olefin substitution is more efficient with ethylene than cyclohexene is attributable to the known greater binding ability of the former olefin to transition metals.[13]

Direct evidence for the loss of an olefin from the original acyl complex in the course of the olefin substitution reaction was obtained when **2i** was reacted with C_2H_4 for 12 h in $CDCl_3$ at 25 °C. As shown in eq 10, 95% of **2i** was converted to **2b**. In addition, all four methylcyclohexene isomers were detected by ^1H NMR spectroscopy, with methylenecyclohexane being the major product.



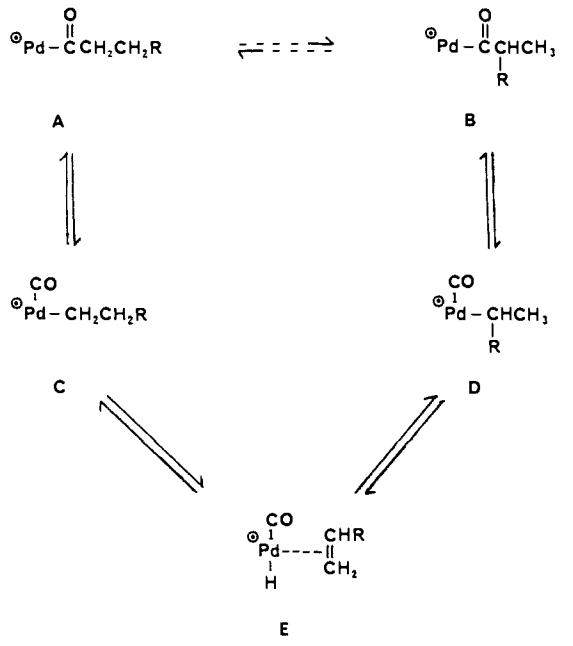
Finally, both **2g** and **2h** reacted with cyclohexene in $CDCl_3$ to produce **2n** in accordance with eq 11. Thus, it appears likely that **2n** was generated from **2g** and **2h** via the replacement of isobutylene by cyclohexene in a common intermediate.



(12) A preliminary report of this observation has appeared, see: Gretz, E.; Sen, A. *J. Am. Chem. Soc.* **1986**, *108*, 6038.

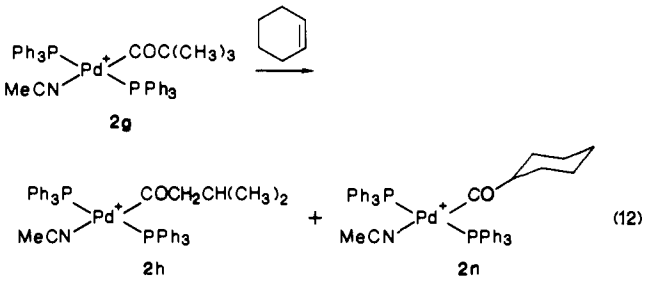
(13) Review: Hartley, F. R. *Chem. Rev.* **1973**, *73*, 163.

Scheme I



E. Kinetics. Due to complications arising from the formation of the starting material via the reverse reaction, the isomer systems depicted in eq 5 and 6, as well as the (methylcyclohexyl)acyl system, were not suitable for routine kinetic experiments involving monitoring reactions through at least 3 half lives. The (methylcyclohexyl)acyl system was further complicated by the reversible formation of a large number of acyl isomers.

The isomerization of **2g** in accordance with eq 7 appeared to be more suitable for kinetic studies because of $K_{eq} > 50$. However, this reaction did not follow good first- or second-order kinetics, since the reaction slowed significantly over time. The poor kinetics observed for eq 7 originated from the release into solution of free MeCN, an inhibitor (vide infra), as a result of decomposition en route to equilibrium (see section C). Since isobutylene was detected as a decomposition product, it was surmised that the intermediate most likely responsible for decomposition was an unstable hydrido(olefin)palladium(II) complex, capable of reversibly dissociating its olefin (Scheme I). Upon losing the olefin, the resulting metal hydride decomposes, presumably through several different pathways including reaction with the solvent. To prevent such decomposition, the isomerization of **2g** was carried out in the presence of a large excess of cyclohexene so as to provide a substitute olefin to replace the lost isobutylene. Thus the transformation of **2g** followed eq 12.



Since both eq 7 and 12 proceed through a common hydrido(isobutylene)palladium(II) intermediate, the rate of disappearance of **2g** should be the same for both reactions.

The disappearance of **2g** in the presence of excess C_6H_{10} at 26 °C in $CDCl_3$ was found to obey good first-order kinetics through 3 half-lives (Figure 5). Superimposed on this linear plot (from eq 12) is a nonlinear plot obtained in the absence of C_6H_{10} (from eq 7). A value of 5.57 (22) × 10^{-3} min^{-1} was calculated for k_{obsd} from the slope of the linear plot.

A linear first-order plot was also obtained from the reaction of **2h** with excess C_6H_{10} at 26 °C in $CDCl_3$. However, the calculated value of k_{obsd}, 4.00 (23) × 10^{-3} min^{-1}, does not accurately reflect the rate at which **2h** forms the hydrido(isobutylene)palladium(II) intermediate, since regeneration of **2h** via the reverse reaction occurs simultaneously with the formation of **2n**.

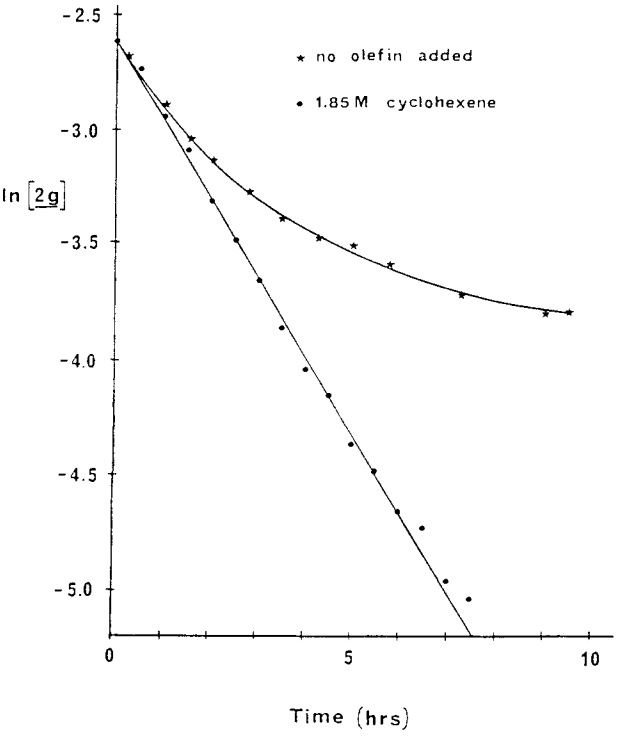


Figure 5. Plots of ln [**2g**] versus time for the isomerization of **2g** in the presence and absence of added cyclohexene.

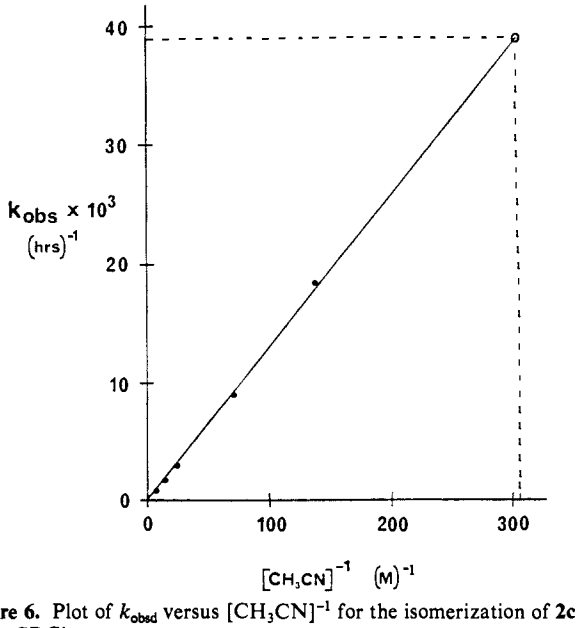


Figure 6. Plot of k_{obsd} versus $[CH_3CN]^{-1}$ for the isomerization of **2c** to **2d** in $CDCl_3$.

The variation of isomerization rate with the concentration of added MeCN was monitored for **2c** in $CDCl_3$. To avoid complications arising from the reverse reaction, the disappearance of **2c** was monitored only over the first one-third of the reaction. Under this condition and based on $K_{eq} = 5.1$ for eq 5, the rate of the reverse reaction never exceeded 10% of the forward reaction rate.

As shown in Figure 6, a plot of k_{obsd} versus $[MeCN]^{-1}$ is linear in the MeCN range of 1.45 × 10^{-1} to 7.27 × 10^{-3} M. The slope and the intercept were calculated from a linear regression analysis to equal 1.38 (8) × 10^{-4} h^{-1} M and −2.0 (68) × 10^{-4} h^{-1}, respectively. Because the line was statistically demonstrated to pass

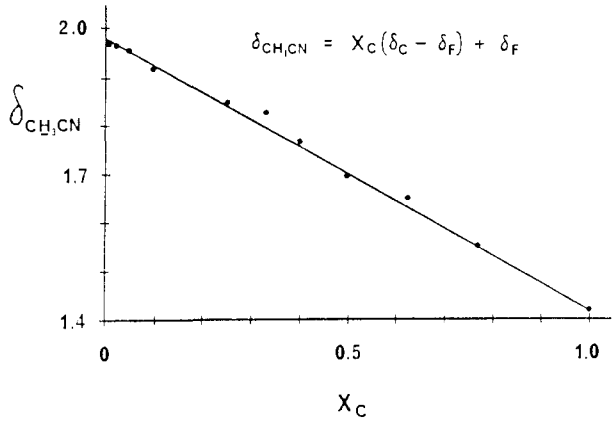
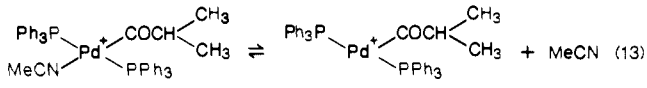


Figure 7. Plot of δ_{CH_3CN} versus mole fraction of coordinated CH_3CN (X_C) for solutions of **2a** containing added CH_3CN.

through the origin, the isomerization obeyed the following rate law: $-d[\mathbf{2c}]/dt = k_{obsd}[\mathbf{2c}][MeCN]^{-1}$.

By extrapolating Figure 6 to $k_{obsd} = 3.98 \times 10^{-2}$ min^{-1} (the observed rate constant in the absence of added MeCN), the concentration of dissociated MeCN in a 0.0464 M solution of **2c** was calculated to be 3.48 (23) $\times 10^{-3}$ M. By using this value, K_{eq} for the dissociative equilibrium shown in eq 13 was found to equal 2.83 (38) $\times 10^{-4}$ M.[14]



IR and ^{1}H NMR experiments employing model compounds that cannot isomerize confirmed that the MeCN dependence arose from the dissociative equilibrium indicated in eq 13. Simultaneously, an associative MeCN dependence involving the formation of an unreactive five-coordinate complex was ruled out. The results of these experiments are described below.

The C≡N stretching region (2500–2000 cm^{-1}) in the IR spectrum of $Pd(PPh_3)_2(MeCN)(COPh)^+BF_4^-$ (**2o**) was monitored in $CHCl_3$ as a function of added MeCN. In the absence of added MeCN, **2o** exhibited bands only at 2305 and 2275 cm^{-1}, corresponding to bound MeCN.[15] As the concentration of added MeCN was progressively increased to 1 M—well beyond that employed in the kinetic experiments—the intensities of these bands did not change. Instead, two bands associated with free MeCN at 2285 and 2251 cm^{-1} were observed to progressively increase in intensity.[16] The absence of any other bands in the region would appear to preclude the formation of any new species in solution.

The conclusion from the IR spectral study was supported by observations derived from the ^{1}H NMR spectra of $Pd(PPh_3)_2(MeCN)(COMe)^+BF_4^-$ (**2a**), in $CDCl_3$. The bound MeCN of **2a** appeared at 1.42 ppm, shifted 0.58 ppm upfield from free MeCN. Addition of MeCN to this solution resulted in a single time-averaged resonance, due to fast MeCN exchange on the NMR time scale. This resonance shifted progressively downfield with increasing concentration of added MeCN in accordance with eq 14, where X_C is the mole fraction of coordinated MeCN and

$$\delta_{MeCN} = X_C(\delta_C - \delta_F) + \delta_F \quad (14)$$

δ_C and δ_F are the chemical shifts of coordinated and free MeCN, respectively. Figure 7 demonstrates the linearity of the plot of δ_{MeCN} versus X_C and is inconsistant with the presence of a significant concentration of a five-coordinate $Pd(PPh_3)_2(MeCN)_2(COR)^+$ species in solution.

Table III. Predicted and Observed Rate Constants for the Formation of **2d** from **2c** in the Presence of Added Triphenylphosphine[a]

$[PPh_3]$ (M)	k_{obsd} (min^{-1})	k_{pred} (min^{-1})[b]
0[c]	3.9×10^{-2}	
0.1	1.4×10^{-2}	1.6×10^{-2}
0.2	1.1×10^{-2}	1.1×10^{-2}
0.4	0.8×10^{-2}	0.7×10^{-2}
0.5	0.4×10^{-2}	0.6×10^{-2}

[a] [**2c** + **2d**] = 0.047 M in $CDCl_3$. Temperature = 26 °C. [b] Calculated from concentration of free CH_3CN in solution, as described in the Kinetics section. [c] Actual concentration was greater than zero, due to phosphine dissociative equilibrium.

As is evident from Table III, the isomerization of **2c** was also inhibited by the addition of Ph_3P. However, even over the first one-third of the reaction, good first-order kinetics were not observed. Some insight into the cause of this strange behavior was obtained from ^{31}P NMR spectroscopic observations on the model compound, **2a**, in the presence of added Ph_3P. The advantage of studying **2a** lies in its inability to undergo isomerization, thus minimizing the number of species formed from interaction with PPh_3.

The ^{31}P NMR spectrum of a mixture of **2a** (0.053 M) and PPh_3 (0.033 M) in $CDCl_3$ at 25 °C consisted only of a very broad resonance (~7 ppm wide at half-height) in the general region expected for either a cationic or neutral Pd(II)–acyl complex. On cooling to −45 °C, several new resonances, in addition to those expected for **2a** and free PPh_3, were observed.

One of those resonances was subsequently identified as the corresponding neutral compound, **1a**, which gradually grew in at the expense of **2a**. Further experiments indicated that the rate of formation of **1a** from **2a** increased with increasing concentration of added PPh_3. Thus, by some unknown mechanism, free PPh_3 catalyzes the formation of **1a** from **2a**, presumably through reaction with $CDCl_3$.

Also present in the low-temperature ^{31}P NMR spectrum were several other resonances whose identities could not be determined. The addition of an excess of MeI (a phosphine sponge) to this solution caused all the unidentified resonances to disappear; only those attributable to **1a**, **2a**, and $PPh_3Me^+I^-$ remained. Thus, the added PPh_3 (a) catalyzes the formation of neutral products from the corresponding cationic Pd(II)–acyl complexes and (b) reversibly forms new species from the latter complexes.

Consistent with the results of the studies on the model compound, **2a**, was the detection of significant amounts of the neutral acyls, **1c** and **1d**, in the isomerization of **2c** in $CDCl_3$ in the presence of an excess of PPh_3. The formation of the neutral complexes from the corresponding cationic species results in the release of MeCN previously bound to the cationic species into the reaction solutions. Since MeCN is a known inhibitor for the isomerization reaction, it was necessary to calculate the contribution of this factor to rate inhibition. The ^{1}H NMR chemical shifts of the MeCN resonance were measured in solutions of **2c** containing known concentrations of added PPh_3. The concentrations of free MeCN were then calculated by using Figure 7. Plugging these numbers into Figure 6 allowed the prediction of rates, based solely on MeCN dependence. The predicted (k_{pred}) and observed (k_{obsd}) rate constants for varying concentrations of added PPh_3 are presented in Table III. The close agreement between these values implies that, for the most part, the rate inhibition caused by added Ph_3P is attributable to the release of free MeCN into the reaction solution. Finally, the occurrence of eq 15 indicates that at least some contribution to the rate inhibition by added PPh_3 may arise from a phosphine dissociative reaction pathway.

F. Temperature Dependence of K_{eq}. The variation of the equilibrium constant for the ^{i}Pr–^{n}Pr system (eq 5) as a function of temperature was determined between 50 and −15 °C. Beyond these extremes it was not possible to measure K_{eq}, since the system

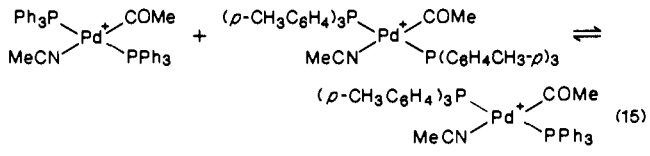
(14) This calculation assumes the absence of a parallel pathway involving phosphine dissociation. Although the addition of Ph_3P does slow the isomerization, the rate inhibition is attributable to other factors (vide infra). A second assumption is that **2c** and **2d** have similar values for K_{eq}.

(15) Two absorption bands are normally observed for both free and coordinated MeCN.

(16) For σ-bonded RCN complexes, the ν(C≡N) values are generally higher than the corresponding free RCN. Review: Storhoff, B. N.; Lewis, H. C. *Coord. Chem. Rev.* **1977**, *23*, 1.

(17) Review: Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395.

(18) Examples from Ir chemistry: Olgemoller, B.; Beck, W. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 834.



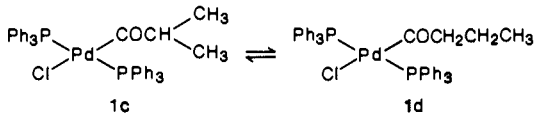
(15)

rapidly decomposed at higher temperatures and established equilibrium too slowly at lower temperatures. From the van't Hoff plot (Figure 8), values of −0.7 (2) kcal/mol and 0.9 (6) cal/(mol K) were calculated for ΔH and ΔS, respectively.

G. Isomerization of Neutral Pd(II)–Acyl Complexes. Having explored the spontaneous isomerization of the cationic Pd(II)–acyl complexes, we sought to extend this type of reaction to the corresponding neutral analogues.

The neutral complexes of the general formula *trans*-$Pd(PPh_3)_2(Cl)(COR)$ did not spontaneously isomerize in solution. For example, a solution of $Pd(PPh_3)_2(Cl)(CO^iPr)$ (**1c**) remained virtually unchanged in $CDCl_3$ after 1 week at 25 °C. Beyond that time, the complex slowly decomposed, principally forming $Pd(PPh_3)_2Cl_2$. Heating a solution of **1c** at 50 °C simply accelerated the rate at which $Pd(PPh_3)_2Cl_2$ was formed. In neither case was the formation of $Pd(PPh_3)_2(Cl)(CO^nPr)$ (**1d**) detected by ^1H or ^{31}P NMR spectroscopy.

Two types of catalysts proved capable of isomerizing **1c** to an equilibrium mixture of **1c** and **1d** (eq 16). The first such catalyst discovered was one of the cationic Pd(II)–acyl complexes pre-



(16)

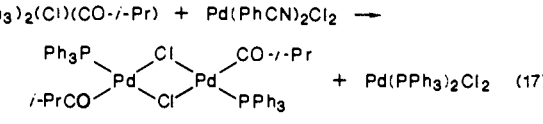
viously found to undergo the spontaneous isomerization reaction. When an equimolar mixture of **1c** and **2c** was allowed to react in $CDCl_3$ at 25 °C for 2 days, the ^{31}P NMR spectrum of the product solution at 25 °C contained only a very broad resonance. However, upon cooling the probe to −45 °C, four very distinct singlets, attributable to **1c**, **1d**, **2c**, and **2d**, were observed. Integration of the signals indicated that both the **1c**:**1d** and **2c**:**2d** ratios were approximately 1:5. Thus, **2c** not only underwent spontaneous isomerization but also catalyzed the isomerization of **1c** to **1d**.

When the reaction was repeated with a 10:1 ratio of **1c** to **2c**, isomerization of both starting materials to their respective equilibrium mixtures was again observed, thus confirming the catalytic behavior of **2c**. In addition, it was qualitatively observed that the rate of isomerization of the neutral complex was proportional to the amount of the cationic species present.

The catalytic isomerization of the neutral Pd(II)–acyl complexes was demonstrated for several catalysts of the general formula *trans*-$Pd(PPh_3)_2(MeCN)(COR)^+BF_4^-$. For example, **2a** (R = Me) and **2o** (R = Ph), both of which cannot isomerize themselves, were observed to catalyze the isomerization of **1c** to **1d**. As was the case with **2c**, the rate of isomerization was dependent on the catalyst concentration.

A second type of catalyst capable of isomerizing the neutral Pd(II)–acyl complexes is a strong Lewis acid, such as $AlCl_3$ or SnF_4. When 1 equiv of $AlCl_3$ was added to a $CDCl_3$ solution of **1c** at 25 °C, the solution color changed from faint yellow to bright yellow. Moreover, the reaction mixture was homogeneous, even though $AlCl_3$ is virtually insoluble in $CDCl_3$. The ^1H NMR spectrum of the solution, although broad, did indicate the formation of a Pd(II)–CO^nPr species. This was confirmed by morpholine cleavage of the acyl group followed by gas chromatography of the resultant amides, which indicated a 5:1 ratio for *n*-butyryl and isobutyryl amides. The isomerization of **1c** to **1d** was also catalyzed by SnF_4. As with the cationic Pd(II)–acyl catalysts, the isomerization rate was proportional to the Lewis acid concentration.

The attempted isomerization of **1c** by abstraction of a phosphine ligand with 0.5 equiv of $Pd(PhCN)_2Cl_2$ resulted in the quantitative formation of a chloro-bridged dimer (eq 17). The dimer was isolated and subsequently heated (60 °C in $CDCl_3$, 80 °C in $PhNO_2$), but no isomerization was observed. Rather the complex decomposed to metallic palladium plus unidentified organic products.



(17)

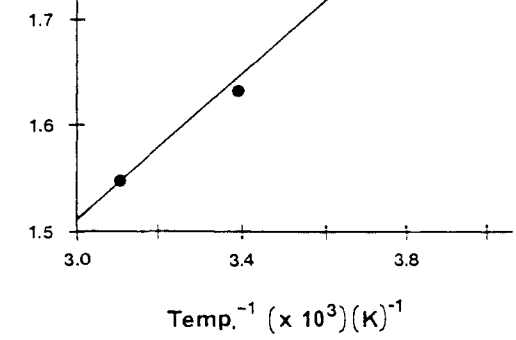


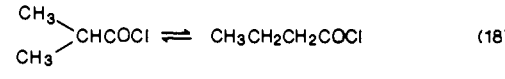
Figure 8. Van't Hoff plot for the isomerization of **2c** to **2d**.

Table IV. Isomerization of Organic Carboxylic Acid Chlorides[a]

entry	catalyst[b]	RCOCl[c]	equiv	[i]/[n]	turnovers[d]
1	**1c** + $AlCl_3$	i	20	2.0	6.7
2	**1c** + $AlCl_3$	n	20	1.8	12.9
3	none	i	20		0
4	**1c**	i	20		0
5	$AlCl_3$	i	20		0
6	**1a** + $AlCl_3$	i	20	2.0	6.7
7	**1a** + $AlCl_3$	n	20	0.9	9.6
8	$Pd(PPh_3)_2Cl_2$	i	20		0
9	$AlCl_3$ + $Pd(PPh_3)_2Cl_2$	i	20		0
10	**2c**	i	20	2.2	6.3
11	**2c**	i	10	1.9	3.5
12	**2c**	n	10	1.8	6.3

[a] 50 °C for 7 days. [b] Catalyst concentration: 0.12 M. [c] Initial acid chloride: i, isobutyryl chloride; n, *n*-butyryl chloride. [d] Moles of acid chloride per mole of catalyst per 7 days.

H. Catalytic Isomerization of Carboxylic Acid Chlorides. Finally, we were able to extend the reaction system to include the catalytic isomerization of carboxylic acid chlorides. The results of our experiments for the interconversion of isobutyryl and *n*-butyryl chloride (eq 18) are presented in Table IV.

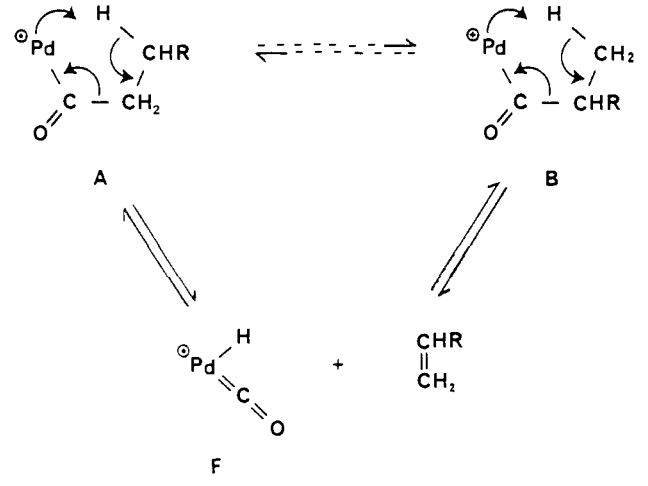


(18)

At 50 °C, an equimolar mixture of **1c** and $AlCl_3$ was found to catalyze the isomerization of isobutyryl chloride to *n*-butyryl chloride (entry 1). We observed 6.7 turnovers, representing the conversion of one-third of the branched isomer. Entry 2 presents the isomerization of *n*-butyryl chloride. In this case, a turnover of 12.9 was observed with the final product mixture again consisting of the branched and the straight chain isomers in the ratio of ~2:1. These experiments clearly indicate that the equilibrium can be reached starting with either of the isomeric acid chlorides.

No isomerization was observed when isobutyryl chloride was heated separately in the presence of **1c** or $AlCl_3$ (entries 4 and 5, respectively). Thus, only the combination of **1c** and $AlCl_3$ was an effective catalyst. The equilibration of isobutyryl and *n*-butyryl chlorides was also catalyzed by a combination of $AlCl_3$ and Pd-$(PPh_3)_2(Cl)(COMe)$ (**1a**) (entries 6 and 7). This indicated that

Scheme II

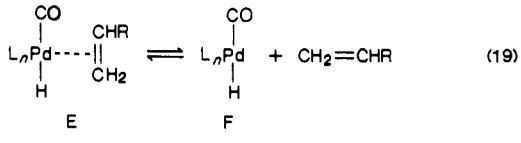


any combination of $AlCl_3$ and a Pd(II)–acyl species of the type $Pd(PPh_3)_2(Cl)(COR)$ was an effective catalyst for the isomerization reaction. Entries 8 and 9 demonstrate that neither $Pd(PPh_3)_2Cl_2$ nor a combination of $Pd(PPh_3)_2Cl_2$ and $AlCl_3$ were effective as catalysts. Finally, the cationic Pd(II)–acyl complex, **2c**, itself was an active catalyst for the isomerization reaction (entries 10–12).

Discussion

The isomerization of cationic Pd(II)–acyl complexes could conceivably take place via either a stepwise or a "concerted" mechanism (Schemes I and II, respectively). In Scheme I, a hydridocarbonylpalladium(II)–olefin intermediate, E, is formed by the deinsertion of CO followed by a β-hydrogen abstraction step. In Scheme II, a hydridocarbonylpalladium(II) intermediate, F, is generated in a concerted process that is initiated through an agostic interaction[17] between the metal and a γ-H atom. Reversal of either process would then generate the isomeric Pd(II)–acyl complexes, A and B, eventually forming the equilibrium mixture.

Both mechanisms involve the formation of a hydridocarbonylpalladium(II) intermediate, differing only in whether or not the olefin remains coordinated to the metal. It is not likely that this difference has much physical significance, since both the intermediates are easily interrelated through eq 19. Complexes



(19)

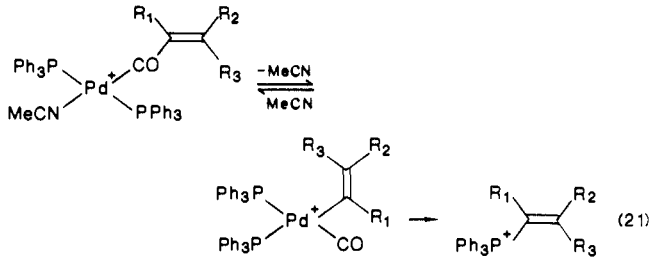
such as E and F have been prepared for other transition metals[18] but have never been isolated for palladium. Therefore, it is not surprising that an intermediate such as E or F was never directly observed in the isomerization reactions.

Several experimental observations, however, provide indirect evidence for the involvement of such intermediates. First, isobutylene was detected as a byproduct in the isomerization of **2g** to **2h**. Second, **2b** and **2n** were formed when the isomerization of **2c** was carried out in the presence of C_2H_4 and cyclohexene, respectively (eq 9). Finally, a small quantity of $CHDCl_2$ was detected in the equilibration of **2c** and **2d**. It is reasonable to assume that this product was formed by the reaction of the solvent, $CDCl_3$, with a Pd(II)–hydride intermediate (eq 20), as has been previously observed for other metal–hydride complexes.[19]

$$L_nPd\text{–}H + CDCl_3 \rightarrow L_nPd\text{–}Cl + CHDCl_2 \qquad (20)$$

On the basis of ^1H NMR spectroscopy, Scheme II seems an attractive possibility. The protons bonded to the γ-carbon of the acyl ligands resonate substantially farther upfield than would normally be predicted. This unusual shielding is consistent with the existence of an agostic interaction between those protons and the metal center. However, organic ligands bound to other metal–phosphine complexes have demonstrated similar behavior, which was not attributed to agostic interactions. Rather, the upfield resonances were attributed to the geometrical placement of these protons within the shielding region of the phenyl rings of the phosphine ligands.[20] Such a phenomenon probably operates in these complexes as well, since (a) the protons attached to the β- and δ-carbons, when present, also resonate farther upfield than would normally be predicted and (b) the corresponding neutral palladium–acyl complexes demonstrate similar ^1H NMR spectral behavior, yet do not undergo isomerization. Complementing the latter point is a crystal structure of **1d**,[21] which clearly demonstrates that the protons of the *n*-butyryl group do not lie within bonding distance of the metal center. Further evidence against an agostic interaction comes from the ^1H-coupled ^{13}C NMR spectrum of **2h** (Table IC). A low $J_{C\text{-}H}$ value (<100 Hz) is expected for the —CH= group if an agostic interaction is present.[17] However, a normal coupling constant of 129 Hz was observed. Thus, despite the unusual upfield chemical shifts in the ^1H NMR spectra of these compounds, the experimental evidence as a whole eliminates the involvement of an agostic interaction between the γ-H's and the Pd(II) center and, consequently, rules out Scheme II.

The isomerization of the cationic Pd(II)–acyl complexes, therefore, presumably proceeds by the mechanism depicted in Scheme I.[22] A slight modification of the pathway shown would conveniently account for the decomposition of the cationic Pd(II)–(vinyl)acyl complexes to the respective vinyltriphenylphosphonium salts, (eq 8). Following the deinsertion of CO, the phosphonium salts were presumably formed by the reductive elimination of the mutually cis PPh_3 and vinyl groups, (eq 21).[23] Mechanistically, therefore, the isomerization and decomposition



(21)

reactions differ only in the fates of the respective Pd(II)–hydrocarbyl intermediates—the alkyls undergoing reversible β-hydrogen abstraction to generate intermediate E and the vinyls, lacking accessible β-hydrogens, irreversibly forming phosphonium salts. Incidently, the "concerted" mechanism shown in Scheme II is inconsistent with the formation of the phosphonium salts.

At least one of the auxillary ligands present on the metal must dissociate prior to the formation of intermediate E so as not to violate the 18-electron rule. Several arguments and experimental observations support MeCN (rather than PPh_3) being the dissociating ligand. MeCN does not bind as strongly to Pd(II) as does PPh_3. Also, the strong trans effect of the acyl group should labilize the trans MeCN ligand. Consistent with these arguments was the observation of a strong retardation of the isomerization rate by added MeCN. For example, no isomerization (or the formation of phosphonium salts for the (vinyl)acyl compounds) was observed when MeCN was used as the solvent, and even the

(19) This is a well-documented reaction. For a few specific examples, see: (a) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650. (b) Janowicz, A. H.; Bergmann, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352.

(20) Bennett, M. A.; Charles, R.; Mitchell, T. R. B. *J. Am. Chem. Soc.* **1978**, *100*, 2737.

(21) Bardi, R.; Del Pra, A.; Piazzesi, A. M.; Tonolio, L. *Inorg. Chim. Acta* **1979**, *35*, L345.

(22) A similar mechanism also operates for the well-known isomerization of transition-metal alkyls. For the most recent examples, see: Bennett, M. A.; Crisp, G. T. *Organometallics* **1986**, *5*, 1792, 1800.

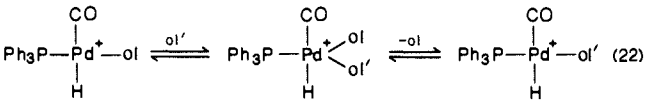
(23) The reductive elimination of the phosphonium cation has been observed previously, see: Kampmeier, J. A.; Harris, S. H.; Rodehorst, R. M. *J. Am. Chem. Soc.* **1981**, *103*, 1478 and references therein.

addition of 1 equiv of MeCN to a Pd(II)–acyl complex slowed the isomerization by approximately an order of magnitude. In addition, the MeCN inhibition was determined by IR and ^1H NMR experiments (Results, section E) to result from a dissociative rather than an associative equilibrium. Unfortunately, however, the experimental evidence does not distinguish between whether the MeCN dissociation occurs before going from A to C or C to E.

The role of the PPh_3 ligands in the reaction pathway is less clear. The observed phosphine exchange (eq 15) demonstrates the lability of the phosphine ligands in these complexes. Thus, the isomerization may potentially take place via a PPh_3 dissociative route, in addition to one involving MeCN dissociation. However, the magnitude of rate retardation by added PPh_3 is substantially smaller than that observed for added MeCN, suggesting that the MeCN-dependent pathway predominates. In addition, as Table III indicates, most of the rate inhibition caused by added Ph_3P can be attributed to the release of free MeCN in solution due to the conversion of the cationic species into the corresponding neutral chloro complexes (Results, section E).

In a molecular orbital analysis of the insertion of C_2H_4 into a Pt(II)–H bond, it was concluded that the insertion process is energetically more favorable for a 4-coordinate than a 5-coordinate complex.[24] Consequently, according to the principle of microscopic reversibility, the reverse process, β-hydrogen abstraction, would be more facile for a 3-coordinate than a 4-coordinate species. Several experimental investigations of the mechanism of β-hydrogen abstraction from d^8, square-planar Pt(II)–[25] and Au(III)–alkyl[26] complexes have yielded the same conclusion. On the basis of these results, it may be reasonable to assume a 4-coordinate structure for the intermediate E, formed by the dissociation of a PPh_3 ligand.

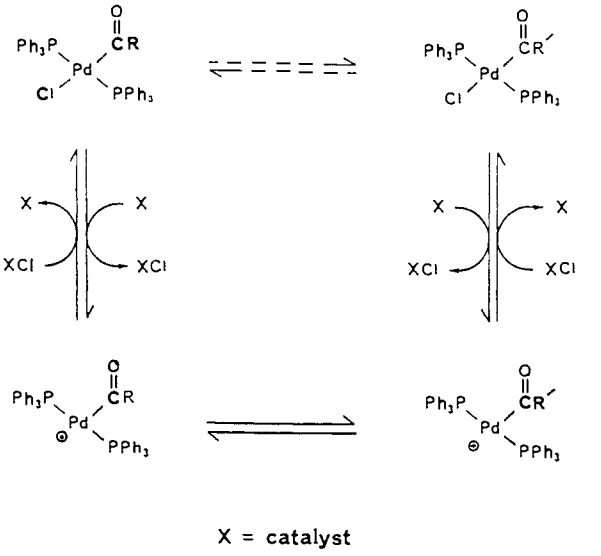
The proposed 4-coordinate structure for intermediate E also accommodates the olefin substitution data (Results, section D), since such an intermediate allows for an associative exchange via an 18-electron complex (eq 22). Although an alternative dissociative mechanism cannot be completely eliminated, two experimental observations are more consistent with an associative exchange pathway.



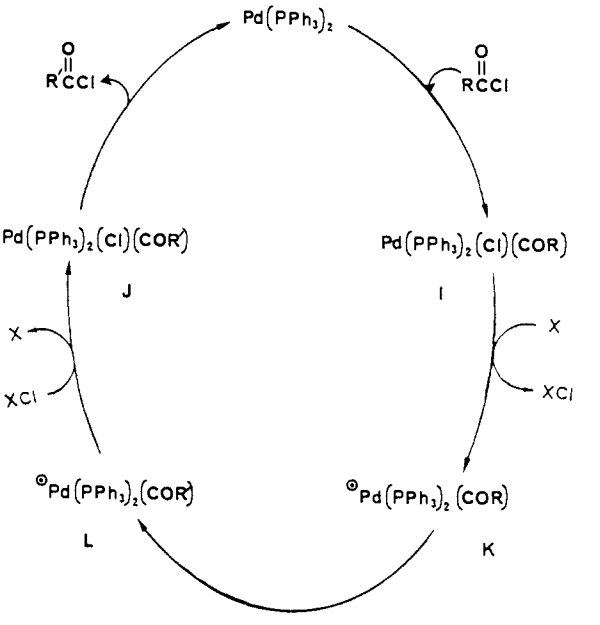
First, the release of the gaseous olefin, C_3H_6, into solution during the isomerization of **2c** and **2d** should eventually lead to the loss of C_3H_6 from the system into the atmosphere. The resulting metal species, $Pd(PPh_3)_2(CO)(H)^+$, would be expected to be unstable and decompose rapidly in solution. However, even after 1 week at 25 °C, only ~10% of the reaction mixture was observed to decompose. This appears to be an unusually small amount, given the dynamic equilibrium involved and the fast rate of ethylene for propylene exchange.

Second, the significantly different rates for ethylene and cyclohexene incorporation into **2c** are not consistent with a dissociative exchange process. After 1 h, ~90% of C_3H_6 from **2c** was displaced by C_2H_4, whereas less than 50% was displaced by cyclohexene after 16 h, even though the solution concentration of C_6H_{10} was far higher than that of C_2H_4. The rate of olefin exchange would be expected to be independent of the nature and the concentration of the incoming olefin for a dissociative process. On the other hand, if an associative mechanism was operating, the exchange rate will depend on the binding ability of the incoming olefin, and C_6H_{10} is known to be a poorer ligand than either C_2H_4 or C_3H_6.[13]

Scheme III



Scheme IV



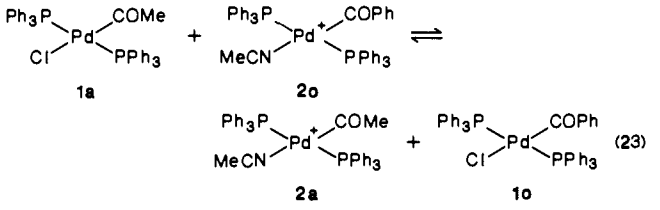
The inability of the neutral Pd(II)–acyl complexes, *trans*-$Pd(PPh_3)_2(Cl)(COR)$, to undergo spontaneous acyl group isomerization must, at least in part, be due to the absence of any easily dissociable ligand. However, the isomerization in these compounds can be induced by a catalytic amount of either a cationic Pd(II)–acyl species, *trans*-$Pd(PPh_3)_2(MeCN)(COR)^+$, or a Lewis acid such as $AlCl_3$. In either case, the role of the catalyst appears to involve the generation of a cationic intermediate from the corresponding neutral Pd(II)–acyl species by halide abstraction. It is this transient cationic Pd(II)–acyl species that then undergoes the isomerization reaction. In the final step, the isomerized cationic Pd(II)–acyl intermediate is reconverted to the corresponding neutral compound by halide abstraction, either from the catalyst or a second neutral Pd(II)–acyl compound. The complete mechanism is shown in Scheme III. Consistent with this mechanism is the observed Cl^- exchange between the neutral and the cationic Pd(II)–acyl complexes, **1a** and **2o**, leading to an equilibrium mixture of **1a**, **2a**, **1o**, and **2o** (eq 23).

A possible mechanism for the isomerization of carboxylic acid chlorides, catalyzed by a combination of *trans*-$Pd(PPh_3)_2(Cl)$-

(24) Thorn, D. L.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 2079. Experimental results also support the intermediacy of four-coordinate species in insertions involving Pd(II) complexes, see: Samsel, E. G.; Norton, J. R. *J. Am. Chem. Soc.* **1984**, *106*, 5505.

(25) (a) Komiya, S.; Morimoto, Y.; Yamamoto, A.; Yamamoto, T. *Organometallics* **1982**, *1*, 1528. (b) Chaudhury, N.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1976**, 915. (c) Whitesides, G. M.; Gaasch, J. F.; Stedronsky, E. R. *J. Am. Chem. Soc.* **1972**, *94*, 5258.

(26) Tamaki, A.; Magennis, S. A.; Kochi, J. K. *J. Am. Chem. Soc.* **1974**, *96*, 6140.



(COR) and $AlCl_3$, is presented in Scheme IV. Following reductive elimination of R'COCl, the reactive species, $Pd(PPh_3)_2$, is formed. Oxidative addition of the acid chloride to this species produces I, which isomerizes to J by the mechanism shown in Scheme III. Reductive elimination then produces the isomerized acid chloride and regenerates $Pd(PPh_3)_2$, thus completing the catalytic cycle. Since the isomerization of butyryl chloride proceeded much more slowly than the corresponding isomerization of **2c** by $AlCl_3$, it appears that the reductive elimination of R'COCl from J constitutes the slow step in Scheme IV. We note, however, that the reductive elimination of acyl halide from a Pd(II) complex has never been demonstrated.

There are two possible mechanisms for the isomerization of acid chlorides catalyzed by the cationic Pd(II)–acyl complexes, $Pd(PPh_3)_2(MeCN)(COR)^+BF_4^-$. The first involves that shown in scheme IV, with the initiation step in eq 24. The BF_3 thus

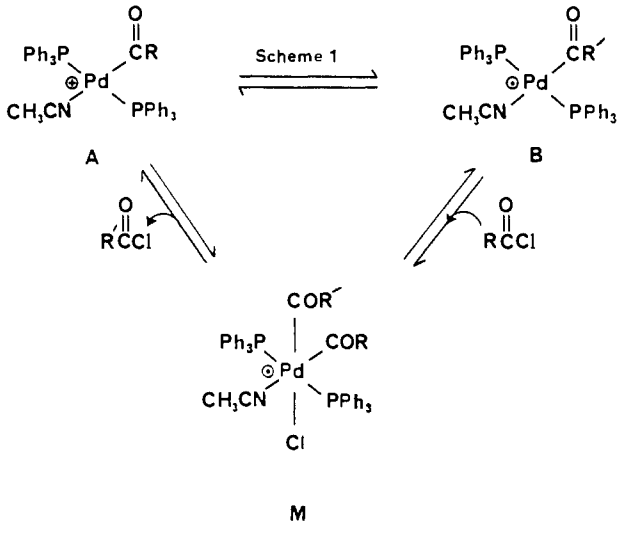
$$Pd(PPh_3)_2(MeCN)(COR)^+BF_4^- \rightarrow Pd(PPh_3)_2 + RCOF + BF_3 + MeCN \quad (24)$$

generated performs the same role as $AlCl_3$ in the previous system. A second mechanism would involve a Pd(IV) intermediate as depicted in Scheme V. The cationic Pd(II)–acyl compound, A, is isomerized to B in accordance with Scheme I. Oxidative addition of RCOCl to B followed by reductive elimination of R'COCl from the resultant Pd(IV) intermediate, M, then completes the cycle. However, a problem with the latter mechanism is the known instability and rarity of Pd(IV) complexes,[27a] although reductive elimination from Pd(IV) intermediates has been previously proposed.[27b]

In the equilibration of the Pd(II)–acyl complexes, the thermodynamically favored isomer was the one with the least branching in the acyl ligand. In contrast, the more stable carboxylic acid chloride is the one with greater branching. For example, at 50 °C, isobutyryl chloride was found to be 0.4 kcal/mol *more stable* than *n*-butyryl chloride, whereas the Pd(II)–isobutyryl species was 1.0 kcal/mol *less stable* than the Pd(II)–*n*-butyryl species—both for the cationic and the neutral compounds. Clearly, this reversal must be due to the greater steric interaction between the acyl group and the PPh_3 ligands in the branched acyl complexes.

Some of the steric congestion associated with these complexes is presumably relieved through a lengthening of the respective Pd–COR bonds.[28,29] Thus, the ΔH_{rxn} of 0.7 kcal/mol associated with eq 5 may be thought to reflect the difference in Pd–COR bond energies between **2c** and **2d**. However, part of this enthalpic difference may also arise from a lengthening of the Pd–PPh_3 bonds. Since it is not possible to separate these contributions, that portion of ΔH_{rxn} arising solely from the difference in the respective Pd–COR bond energies of **2c** and **2d** cannot be accurately determined. In general, any experimentally determined metal–carbon bond dissociation energy must be considered in the specific context of

Scheme V



that particular metal complex. Specific metal–carbon bonds of complexes having ligands of different steric bulk are known to have different bond dissociation energies.[30]

A second consequence of steric repulsions in Pd(II)–acyl complexes would be a decrease in the entropy due to the loss of rotational degrees of freedom from sterically induced barriers. While the entropy difference between isobutyryl and *n*-butyryl radicals is not known accurately, the isopropyl radical is estimated to have 1 cal/(mol K) *more* entropy than the *n*-propyl radical, using Benson's method of group contributions.[31] In contrast, the measurement of ΔS_{rxn} for eq 5 shows that the Pd(II)–isobutyryl species has ~0.9 cal/(mol K) *less* entropy than the corresponding Pd(II)–*n*-butyryl species, thus indicating a modest change in the relative entropy difference between these groups upon coordination to a Pd(II) center. Experimentally, the existence of restricted rotation about the Pd–COR bond in the isobutyryl complex, **2c**, was indicated by the presence of two carbonyl absorptions in its IR spectrum.[32] On the other hand, only one carbonyl band is observed for the *n*-butyryl compound, **2d**.

Finally, the equilibrium constants and $\Delta\Delta G°_f$ values had never been experimentally determined for isomeric carboxylic acids or acid chlorides, due to the absence of a known method for the equilibration of the isomers. Until now, these values could only be evaluated theoretically, e.g., by using Benson's tables for group contributions.[31] As such, a fairly large error was introduced since a very small number was obtained by the subtraction of one large number from another (the $\Delta G°_f$ values for the isomers). In the specific case of isomeric butyryl chlorides (eq 18), K_{eq} and $\Delta\Delta G°_f$ were experimentally determined to be 1.85 (5) and −0.40 (2) kcal/mol, respectively, at 50 °C. By using Benson's tables, the calculated values obtained were 16.99 and −1.83 kcal/mol respectively.[33] Although the difference in $\Delta\Delta G°_f$ between experimental and calculated values is only ~1.4 kcal/mol, this translates to a factor of ~10 in the difference in K_{eq}. Thus, the Pd-catalyzed isomerization of organic acid chlorides provides the most accurate method presently known for the determination of the relative free energies of formation for such compounds and, by extrapolation, for other isomeric acyl and alkyl derivatives.

(27) (a) Hartley, F. R. *The Chemistry of Platinum and Palladium*; Wiley: New York, 1973. (b) Moravskiy, A.; Stille, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 4182. Gillie, A.; Stille, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4933. Milstein, D.; Stille, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 4981.

(28) The failure to synthesize ^{i}Pr– and ^{t}Bu–Pd(II) complexes, after the successful synthesis of the analogous straight-chain isomers led others to the same conclusion, see: Ozawa, F.; Ito, T.; Yamamoto, A. *J. Am. Chem. Soc.* **1980**, *102*, 6457.

(29) Long M–C bonds have been observed in the crystal structures of other sterically crowded complexes. Examples: (a) Jeffrey, J.; Lappert, M. L.; Luong-Thi, N. T.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Chem. Commun.* **1978**, 1081. (b) Randaccio, L.; Bresciani-Pahor, N.; Toscano, P. J.; Marzilli, L. G. *J. Am. Chem. Soc.* **1980**, *102*, 7372.

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Experimental Section

A. General Considerations. All reactions were prepared in a N_2-filled glovebox, where all reagents were stored. All solvents, including NMR solvents, were dried over calcium hydride, except for benzene, which was dried over sodium benzophenone ketyl. Once dry and deoxygenated, the solvents were stored in brown bottles in the glovebox.

Cyclohexene (Aldrich) and cyclopentene (Aldrich) were vacuum distilled prior to use, while morpholine (Alfa), norbornylene (Aldrich), and norbornadiene (Aldrich) were used as received without purification. Ethylene (Matheson-CP Grade) was used directly from the cylinder. Acetyl chloride, propionyl chloride, isovaleryl chloride, pivaloyl chloride, crotonyl chloride, and cyclohexanoyl chloride (all Aldrich) were distilled prior to use, while 2-methylbutanoyl chloride, 1-methylcyclohexanoyl chloride, cyclohexylacetyl chloride, and cyclopentanoyl chloride were distilled following their syntheses from the corresponding carboxylic acids (all Aldrich) and thionyl chloride (Alfa). Aluminum trichloride (Aldrich), stannic fluoride (Alfa), and silver tetrafluoroborate (Aldrich) were used as received.

Routine ^1H NMR spectra were recorded in $CDCl_3$ or CD_3CN on either a Varian EM-360 (60 MHz), a Bruker WP-200 (200 MHz), or a Bruker WP-360 (360 MHz) spectrometer. ^{13}C NMR spectra were recorded on the Bruker WP-200 spectrometer. For both nuclei, chemical shifts are reported as δ values relative to tetramethylsilane at 0.00 ppm. ^{31}P NMR spectra were recorded on Varian CFT-20 (32.2 MHz for phosphorus) spectrometer. ^{31}P chemical shifts are reported as δ values relative to 85% H_3PO_4 at 0.00 ppm, with resonances downfield from phosphoric acid being taken as positive.

Infrared spectra were recorded on a Perkin-Elmer Model 580 grating spectrometer, either as Nujol mulls or in chloroform solutions.

Gas chromatography analyses were carried out with either a Varian 3700 or Hewlett Packard 5790 gas chromatograph, both of which were equipped with flame ionization detectors. A 10 ft × $^1/_8$ in. stainless steel column having a 10% SP-2100 packing on 80/100 Supelcoport was employed with the Varian 3700. A 30 m × 0.25 mm DB-5 capillary column was used with the Hewlett Packard instrument. Peak areas were determined by the method of cutting and weighing, except with the Hewlett Packard instrument, which was interfaced with a Hewlett Packard 3390A integrator.

Gas chromatography–mass spectrometry was performed on a system composed of a Finnigan 9500 gas chromatograph, a Finnigan 3200 mass spectrometer, and a Finnigan 6000 mass spectral data system. Impact energy was imparted at 70 eV. In the case of chemical ionization, methane was used as reagent gas. Minimum detection limits were 35 and 60 amu for electron impact and chemical ionization, respectively.

B. Preparation of Palladium Complexes. All the palladium complexes used in this investigation were ultimately synthesized from $PdCl_2$, which was used as received from Johnson-Matthey, Inc. $Pd(PPh_3)_4$ and $Pd[P(p\text{-tolyl})_3]_4$ were prepared by the reduction of $PdCl_2$ by $NH_2NH_2{\cdot}H_2O$, as described by Coulson.[34]

Complexes of the general formulas *trans*-$Pd(PPh_3)_2(Cl)(COR)$ and *trans*-$Pd[P(p\text{-tolyl})_3]_2(Cl)(COR)$ were prepared via the well-known oxidative-addition of carboxylic acid chlorides to $Pd(PPh_3)_4$ and $Pd[P(p\text{-tolyl})_3]_4$, respectively, as reported in the literature.[35] Percentage yields, as well as ^{31}P NMR and IR spectral data, are presented for these complexes in Table IA. ^1H NMR data are displayed in Table IB, while selected ^{13}C NMR data are presented in Table IC.

Compounds of the general formula *trans*-$Pd(PPh_3)_2(MeCN)(COR)^+BF_4^-$ were synthesized in the following way. Approximately 1.0 g of *trans*-$Pd(PPh_3)_2(Cl)(COR)$ was dissolved in a minimum volume (~20 mL) of a 10:1 (v/v) mixture of CH_2Cl_2 and MeCN. To this rapidly stirring solution was added dropwise 1 equiv of $AgBF_4$ dissolved in 1–2 mL of MeCN. The resultant heterogeneous mixture was then filtered, yielding a white residue (AgCl) and a yellow filtrate. The filtrate was immediately added dropwise to rapidly stirring Et_2O at 0 °C, thereby instantaneously precipitating the cationic complex as a white or off-white solid, which was then isolated by filtration. The product was washed with Et_2O and pentane and then dried under vacuum.

Two points concerning the above synthesis are worthy of note. First, the ratio of MeCN to CH_2Cl_2 must be sufficiently high to inhibit isomerization, yet low enough to prevent the formation of an oil when the filtrate is added to Et_2O. Second, removal of the solvent under vacuum caused significant product decomposition. In addition, MeCN became incorporated into the product in undefined stoichiometries (between 1 and 2 per Pd atom). Precipitation in Et_2O, on the other hand, formed a complex containing exactly 1 MeCN/Pd atom.

For the cationic Pd(II)–acyl complexes, the percentage yields, as well as ^{31}P NMR and IR spectral data, are presented in Table IIA. ^1H NMR data are displayed in Table IIB. ^{13}C NMR data for **2h** are given in Table IC.

$Pd(PhCN)_2Cl_2$ was prepared from $PdCl_2$ according to the method of Kharasch.[36] The addition of 2.2 equiv of PPh_3 to this complex in $CHCl_3$ generated $Pd(PPh_3)_2Cl_2$ as yellow crystals. These were isolated in 95% yield by filtration.

The chloro-bridged Pd(II) dimer, $[Pd(PPh_3)(Cl)(CO^iPr)]_2$, was prepared by adding exactly 0.5 equiv of $Pd(PhCN)_2Cl_2$ to a solution of $Pd(PPh_3)_2(Cl)(CO^iPr)$ in CH_2Cl_2.[37] The homogeneous solution instantaneously became heterogeneous. The solution was filtered and the filtrate stirred with pentane. The resultant yellow solid was isolated by filtration and dried under vacuum. Yield: 0.535 g (83%), based on 1.00 g of $Pd(PPh_3)_2(Cl)(CO^iPr)$ starting material. ^1H NMR ($CDCl_3$): 1.2 (d, J = 7 Hz, 12 H), 2.0 (m, J = 7 Hz, 2 H), 7.3–7.9 (m, 30 H) ppm. ^{31}P NMR ($CDCl_3$): 26.65 ppm. IR (Nujol): $\bar{\nu}$(CO), 1705 cm^{-1}.

The above-described synthesis can be extended to include any complex of the general formula $[Pd(PPh_3)(Cl)(COR)]_2$. Reactions for R = Me, Et, and Ph were carried out in ^{31}P NMR tubes in $CDCl_3$. The dimeric products were produced quantitatively in less than 1 min at 25 °C. They were identified exclusively on the basis of ^{31}P NMR spectroscopy. ^{31}P NMR ($CDCl_3$): 26.58 (R = Me), 26.69 (R = Et), 26.52 (R = Ph) ppm.

C. Isomerization of $[Pd(PPh_3)_2(MeCN)(COR)](BF_4)$ (R = Alkyl). Typically, 0.100 g of Pd(II) complex was dissolved in 1.50 mL of $CDCl_3$, forming a homogeneous pale yellow solution. This was immediately transferred to an NMR tube and sealed with an air-tight rubber septum. The reaction was subsequently monitored by ^{31}P NMR spectroscopy. Alternatively, a solution of 0.035 g of Pd(II) complex in 0.6 mL of $CDCl_3$ was prepared and transferred to an NMR tube and the reaction was monitored by ^1H NMR spectroscopy. Reaction products were characterized by ^1H and ^{31}P NMR spectroscopy and (after reaction with morpholine) by gas chromatography.

During the course of the reaction, the solution gradually darkened in color, initially to dark yellow and later to yellow-brown. Occasionally, trace amounts of $Pd(PPh_3)_2Cl_2$ or metallic palladium were observed, but the amount of decomposition, as determined by ^{31}P NMR spectroscopy, generally accounted for less than 10% of the system. Exposure to air accelerated the rate of decomposition and was thus avoided.

D. Decomposition of $[Pd(PPh_3)_2(MeCN)(COR)](BF_4)$ (R = Vinyl). The reaction solutions were prepared exactly as those for the isomerization described above. Addition of the Pd(II) complex to $CDCl_3$ immediately generated a homogeneous cherry red solution, which became red-purple within 30 s. After 1 day the reactions were observed spectroscopically to be ~90% complete; no further change in physical appearance was noted. With one exception, the vinyl phosphonium salts were not isolated. Rather, they were identified in situ by comparison of their ^1H NMR spectra with those in the literature.[38] The one exception was $PPh_3(CMe{:}CH_2)^+BF_4^-$, which was isolated from the decomposition of **2k**. After the product solution was evaporated to dryness under vacuum, MeOH was added. The heterogeneous solution was allowed to stir at 25 °C for 3 h, after which time the solution was filtered. MeOH was then removed from the pink filtrate, leaving behind a red residue. This residue was dissolved in $CDCl_3$ and determined spectroscopically to be 95% pure phosphonium salt.

E. Isomerization of $Pd(PPh_3)_2(Cl)(CO^iPr)$. 1. Catalyzed by $[Pd(PPh_3)_2(MeCN)(COR)](BF_4)$ (R = ^{i}Pr or Ph). To a solution of 0.050 g (0.068 mmol) of $Pd(PPh_3)_2(Cl)(CO^iPr)$ in 1.5 mL of $CDCl_3$ was added 0.056 g (0.068 mmol) of $[Pd(PPh_3)_2(MeCN)(CO^iPr)](BF_4)$. The mixture was transferred to an NMR tube, which was immediately sealed with a rubber septum. After 24 h at room temperature, the originally yellow homogeneous solution had not changed its physical appearance. The isomeric products were identified by low-temperature (−45 °C) ^{31}P NMR spectroscopy, by ^1H NMR spectroscopy, and, after addition of 0.100 mL (1.1 mmol) of morpholine, by gas chromatography.

The reaction was repeated with other concentrations of **2c**. Also, $[Pd(PPh_3)_2(MeCN)(COPh)](BF_4)$ was substituted for **2c**. Isomerization of the neutral complex was observed in each case.

2. Catalyzed by Lewis Acids. To a solution of 0.060 g (0.081 mmol) of $Pd(PPh_3)_2(Cl)(CO^iPr)$ in 1.5 mL of $CDCl_3$ was added 0.003 g (0.02 mmol) of $AlCl_3$. The homogeneous pale yellow solution immediately became darker yellow, but remained homogeneous. The mixture was transferred to an NMR tube, which was immediately sealed with a

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rubber septum. After 24 h, the appearance of solution had not changed any further. Although the ^{31}P NMR spectrum was too broad, even at −45 °C, to be of any diagnostic value, the ^1H NMR spectrum, even though it too was very broad, indicated that isomerization had taken place. Gas chromatography, after addition of 0.200 mL (2.3 mmol) of morpholine, confirmed the isomerization, as the ratio of 4-butyrylmorpholine to 4-isobutyrylmorpholine in the products was approximately 5 to 1.

The isomerization was also successfully carried out by substituting 0.010 mmol of SnF_4 for $AlCl_3$ and $C_6D_5NO_2$ for $CDCl_3$.

F. Thermal Decomposition of $[Pd(PPh_3)(Cl)(CO^iPr)]_2$. To 0.6 mL of $CDCl_3$ was added 0.026 g (0.027 mmol) of the chloro-bridged dimer, forming a bright yellow homogeneous solution. The mixture was transferred to a ^1H NMR tube, which was immediately sealed with a rubber septum. After 24 h at 25 °C, the solution remained homogeneous and yellow, and its ^1H NMR spectrum had not changed. The solution was then heated at 60 °C for 24 h, after which time a homogeneous orange solution and a Pd mirror had formed. Both ^1H NMR and ^{31}P NMR spectra indicated that decomposition had occurred, but the product(s) could not be identified. However, isomerization of the acyl ligand had clearly not taken place. Analogous results were obtained upon substituting $C_6D_5NO_2$ for $CDCl_3$.

G. Catalytic Isomerization of *n*-Butyryl and Isobutyryl Chlorides. Solutions (total volume = 0.5 mL) of the appropriate catalyst (0.048 g of **1a**, 0.050 g of **1c**, or 0.048 g of $Pd(PPh_3)_2Cl_2$ and 0.009 g of $AlCl_3$, or 0.053 g of **2c**) and the acid chloride (0.142 mL for a 20-fold excess, 0.071 mL for a 10-fold excess) were prepared in $CDCl_3$. The solutions were placed in 5-mm glass tubes, which were transferred without exposure to air from the glovebox to the vacuum line. The tubes were then sealed and placed in a 50 °C oil bath to react. During the course of the reaction, those tubes containing a metal complex became brighter yellow in color. No metallic Pd was ever detected. The solution containing $AlCl_3$ and isobutyryl chloride, but no Pd(II) complex, developed a brown color and released gases when the sealed sample was opened.

After 1 week, the tubes were removed from the heat, cooled to 25 °C, and subsequently opened. The isomerization was established both by ^1H NMR spectroscopy and by gas chromatography. The relative ratios of *n*-butyryl chloride to isobutyryl chloride were determined by integration of their respective peaks from the gas chromatograph. The relative peak areas were not corrected, since in a calibration experiment, an equimolar solution of the isomeric acid chlorides revealed an *n*-butyryl chloride to isobutyryl chloride FID response factor ratio of 1 to 1.05. To within experimental error, this ratio was considered equal to unity.

H. Kinetic Experiments. 1. Reaction Order in the Palladium–Acyl Complex. The reactions were monitored by ^{31}P NMR spectroscopy. For each data point, 120 transients were collected over a sweep width of 800 Hz, employing a pulse delay of 7 s and a pulse width of 4 μs (correlating to a nuclear flip angle of 45°). Peak areas were determined by integration of the Fourier-transformed spectrum without line broadening.

a. $[Pd(PPh_3)_2(MeCN)(CO^tBu)](BF_4)$ + Cyclohexene. 2g (0.100 g, 0.119 mmol) was dissolved in 1.30 mL of $CDCl_3$. The reaction was initiated upon addition of cyclohexene (0.30 mL, 5.0 mmol), after which the solution was immediately transferred to the NMR probe, which was maintained at 26 (1) °C. Data points were then collected every 30 min for 7.5 h.

b. $[Pd(PPh_3)_2(MeCN)(CO^iBu)](BF_4)$ + Cyclohexene. 2h (0.100 g, 0.119 mmol) was dissolved in 1.30 mL of $CDCl_3$. The reaction was initiated upon addition of cyclohexene (0.30 mL, 5.0 mmol), after which the solution was transferred to the NMR probe, which was maintained at 26 (1) °C. Data points were collected every 45 min for 7.5 h.

2. Acetonitrile Dependence. The rate of formation of **2d** from **2c** in the presence of added MeCN was monitored by ^{31}P NMR spectroscopy. To avoid complications arising from the reverse reaction, the disappearance of **2c** was monitored only over the first one-third of the reaction. As such, the rate of the reverse reaction never exceeded 10% of the rate of the forward reaction.

For each data point, 50 transients were collected over a sweep width of 300 Hz, employing a pulse delay of 5 s and a pulse width of 4 μs. Peak areas were determined by cutting and weighing photocopies of the Fourier-transformed spectrum after a 1.000 s sensitivity enhancement. The NMR probe temperature was maintained at 26 (1) °C.

A solution (total volume = 1.3 mL) of **2c** (0.056 g, 0.06 mmol) and the appropriate volume of MeCN was prepared in $CDCl_3$. Data points were taken at selected intervals, depending on the rate of reaction. When not in the probe, the solutions were maintained at 26 (1) °C.

3. Phosphine Dependence. Because added Ph_3P caused both severe broadening in the ^{31}P NMR spectrum and saturation in the ^1H NMR spectrum, the phosphine dependence for the formation of **2d** from **2c** was monitored by gas chromatography, after quenching reaction aliquots with excess morpholine. Quantitative measurements were carried out by integrating the gas-chromatogram peaks of the corresponding amides by using the method of cutting and weighing. The relative peak areas were not corrected, since, in a calibration experiment, an equimolar solution of the isomeric amides revealed a 4-butyrylmorpholine to 4-isobutyrylmorpholine peak area ratio of 0.97 to 1.0. To within experimental error, this ratio was considered unity.

A solution (total volume = 1.5 mL) of **2c** (0.058 g, 0.070 mmol) and the appropriate weight of Ph_3P was prepared in $CDCl_3$. This solution was immediately divided into four equal portions, which were subsequently quenched with morpholine (0.050 mL, 0.57 mmol) at selected time intervals. The solutions were maintained at 26 (1) °C.

I. Olefin Exchange Experiments. 1. Reaction of $[Pd(PPh_3)_2(MeCN)(CO^iPr)](BF_4)$ with Ethylene. To a 10-mL round-bottom flask equipped with a sidearm were added **2c** (0.200 g, 0.24 mmol) and 5 mL of $CDCl_3$. The homogeneous pale yellow solution was immediately frozen under liquid N_2 and placed under vacuum. One atmosphere of C_2H_4 was transferred into the flask, which was then allowed to warm to 25 °C. The flask was occasionally vented to relieve excess gas pressure.

After being stirred for 1 h at 25 °C, the solution remained homogeneous, but became slightly brighter yellow in color. Both the ^1H and ^{31}P NMR spectra of aliquots removed from the solution were consistent with the formation of $[Pd(PPh_3)_2(MeCN)(COEt)](BF_4)$ (**2b**). Integration of the gas chromatogram of the remaining solution, after addition of 0.200 mL (2.3 mmol) of morpholine, revealed that **2b**, **2c**, and **2d** were present in percentages of 90, 2, and 8, respectively. The identities of the corresponding amides were established by gas chromatography–mass spectrometry, after separating the solvent and amides from the now-decomposed metal residue by distillation at 60 °C under reduced pressure (0.001 Torr).

2. Reaction of $[Pd(PPh_3)_2(MeCN)(CO^iPr)](BF_4)$ with Cyclohexene. To a 5-mL round-bottom flask was added **2c** (0.060 g, 0.072 mmol), cyclohexene (0.140 mL, 1.38 mmol), and 1.8 mL of $CDCl_3$. After being stirred at 25 °C for 16 h, no change in the physical appearance of the solution was observed. The reaction was then quenched by addition of morpholine (0.100 mL, 1.1 mmol). The resulting amides, arising from **2c**, **2d**, and **2n**, were present in percentages of 9, 47, and 44, respectively, as determined by gas chromatography. The identities of the amides were established by gas chromatography–mass spectrometry, after separating the solvent and amides from the metal residue by distillation at 60 °C under reduced pressure (0.001 Torr).

3. Reaction of $[Pd(PPh_3)_2(MeCN)(COR)](BF_4)$ (R = 1-Methylcyclohexyl) with Ethylene. The reaction was prepared exactly as that described for the reaction of **2c** with ethylene, except that **2i** (0.300 g, 0.34 mmol) was substituted for **2c**. The solution was stirred at 25 °C for 12 h, during which time the initially homogeneous pale yellow solution became slightly yellow-brown in color. The volatiles were then separated from the nonvolatiles at 25 °C under reduced pressure (0.001 Torr).

Several products, in addition to free ethylene, were identified by a ^1H NMR spectrum of the volatiles. These were methylenecyclohexane,[39] 1-methylcyclohexene,[40a] 3-methylcyclohexene,[40b] and 4-methylcyclohexene,[40c] based on a comparison of the observed vinyl resonances with those reported in the literature for these compounds. The vinyl resonances of 3-methyl- and 4-methylcyclohexenes were indistinguishable. Thus, their relative percentages could not be determined by integration. Combined, they represented 37% of the olefinic products, while methylenecyclohexane and 1-methylcyclohexene accounted for 56% and 7%, respectively.

A ^1H NMR spectrum of the nonvolatiles in $CDCl_3$ indicated that **2b** was the major organometallic product (>95%). This assignment was based on comparison of the spectrum with that of an independently prepared sample of **2b** in $CDCl_3$.

4. Reaction of $[Pd(PPh_3)_2(MeCN)(CO^tBu)](BF_4)$ with Cyclohexene. To a 5-mL round-bottom flask were added **2g** (0.100 g, 0.119 mmol), cyclohexene (0.20 mL, 1.97 mmol), and 1.80 mL of $CDCl_3$. The homogeneous pale yellow solution was stirred for 16 h, after which time morpholine (0.100 mL, 1.1 mmol) was added. The resulting amides and solvent were separated from the now-decomposed palladium residue by distillation at 60 °C under reduced pressure (0.001 Torr). Gas chromatography–mass spectrometry indicated that >95% of the corresponding amides was 4-cyclohexanoylmorpholine.

5. Reaction of $[Pd(PPh_3)_2(MeCN)(CO^iBu)](BF_4)$ with Cyclohexene. The reaction was carried out exactly as that described above, except that **2h** (0.100 g, 0.119 mmol) was used in place of **2g**. Again, >95% of the amides formed after addition of morpholine was 4-cyclohexanoylmorpholine, as determined by GC–MS.

(39) Bhacca, N. S.; Johnson, L. F.; Shoolery, J. N. *NMR Spectra Catalog*; Varian Associates; Vol. 1, No. 180.

(40) *Sadtler Stander Spectra, Proton NMR Collection*; Sadtler Research Laboratories, 1980; (a) No. 3420, (b) No. 21612, (c) No. 17121.

J. Determination of Equilibrium Constants. Values of K_{eq} were calculated only for those systems containing two isomers in equilibrium. To ensure that equilibrium had been reached, at least two measurements were made, one for each direction of approach to equilibrium. Integration of the ^1H NMR or ^{31}P NMR spectrum, integration of the gas chromatograph after quenching with morpholine, or a combination of these techniques was employed.

When ^1H NMR spectroscopy was used, the equilibrium mixture was run with routine parameters. ^{31}P NMR spectra were recorded at −45 °C. Three hundred transients were collected over 800 Hz, with a pulse delay of 7 s and a pulse width of 4 μsec. Peak areas were determined by integration of the Fourier-transformed spectrum without line broadening.

When gas chromatography was employed, the metal–acyl complexes were converted to their corresponding amides by reaction with a large excess of morpholine. The relative peak areas of the amides were determined by cutting and weighing photocopies of the respective peaks. These areas were uncorrected, since equimolar solutions of independently prepared isomeric amides yielded GC response factor ratios of unity to within experimental error.

K. Determination of the Temperature Dependence of K_{eq} for Equation 5. 2c (0.0400 g, 0.48 mmol) was dissolved in 6.0 mL of $CDCl_3$, and equal volumes of the resulting homogeneous solution were transferred into four NMR tubes. The tubes were sealed with rubber septa and allowed to reach equilibrium by sitting for 24 h at 23 °C. One tube each was then allowed to stand at 50, 0, and −15 °C, respectively. The remaining tube was frozen in liquid N_2 and transferred to the ^{31}P NMR spectrometer probe, where it was warmed to −45 °C. A ^{31}P NMR spectrum was run as described above, from which K_{eq} was determined by integration. Morpholine (0.200 mL, 2.3 mmol) was then added to the solution, and K_{eq} was calculated a second time by integration of the resulting gas chromatograph. The other three tubes were analyzed in the exact same manner, after remaining at 50, 0, and −15 °C for 1 h, 1 week, and 3 weeks, respectively. Substantial decomposition was observed in the tube kept at 50 °C, but only slight decomposition was noted in the other samples.

L. Chloride Exchange Reaction: $Pd(PPh_3)_2(Cl)(COMe)$ + $[Pd(PPh_3)_2(MeCN)(COPh)](BF_4)$. 1a (0.10 g, 0.14 mmol) in 1 mL of $CDCl_3$ was added to **2o** (0.12 g, 0.14 mmol) in 1 mL of $CDCl_3$, forming a homogeneous yellow solution. After 24 h, during which time there was no physical change of the solution, a low-temperature (−45 °C) ^{31}P NMR spectrum was run, revealing the presence of **2a** and **1o**, in addition to the starting complexes. All four species were determined to be present in approximately equal concentrations by integration.

M. Phosphine Exchange Reactions. 1. $Pd(PPh_3)_2(Cl)(CO^iPr)$ + $Pd[P(p\text{-tolyl})_3]_2(Cl)(CO^iPr)$. 1c (0.10 g, 0.14 mmol) in 1 mL of $CDCl_3$ was added to **1c*** (0.11 g, 0.14 mmol) in 1 mL of $CDCl_3$, forming a homogeneous yellow solution. After 2 h at 25 °C, a low-temperature (−45 °C) ^{31}P NMR spectrum was run. Singlets at 19.01 and 17.21 ppm were assigned to the starting materials, **1c** and **1c***, respectively, while resonances at 18.09 and 18.15 ppm were assigned to a new complex, $Pd[P(p\text{-tolyl})_3](PPh_3)(Cl)(CO^iPr)$.

The outermost resonances expected for the AX system were not observed, probably because $\Delta\nu/J$ was very small. The two inner peaks were separated by only 1.7 Hz. Given that typical trans ^{31}P–^{31}P coupling constants are several hundred hertz,[41] the assumption that $\Delta\nu/J$ is small seems reasonable.

2. $[Pd(PPh_3)_2(MeCN)(COMe)](BF_4)$ + $[Pd[P(p\text{-tolyl})_3]_2(MeCN)(COMe)](BF_4)$. 2a (0.10 g, 0.12 mmol) in 1 mL of $CDCl_3$ was added to **2a*** (0.11 g, 0.12 mmol) in 1 mL of $CDCl_3$, forming a homogeneous yellow solution. After 2 h at 25 °C, a low-temperature (−45 °C) ^{31}P NMR spectrum was run. Singlets at 19.43 and 17.72 ppm were assigned to the starting materials, **2a** and **2a***, respectively, while resonances at 18.74 and 18.54 ppm were assigned to a new complex, $[Pd[P(p\text{-tolyl})_3](PPh_3)(MeCN)(COMe)](BF_4)$. For the same reason presented above, the outermost resonances expected for this AX system were not observed.

N. IR and ^1H NMR Spectral Investigations of $[Pd(PPh_3)_2(MeCN)(COR)](BF_4)$ in the Presence of Added MeCN. 1. IR Spectroscopy. A solution 0.0667 M in $[Pd(PPh_3)_2(MeCN)(COPh)](BF_4)$ was divided into five equal portions of 0.50 mL each. MeCN concentrations were then made equal to 0.0, 0.10, 0.20, 0.50, and 1.00 M by addition of 0, 2.6, 5.2, 13.0, and 26.0 μL, respectively.

By using a $CHCl_3$ reference cell, an IR spectrum was run for each solution in the region 2000–2500 cm^{-1}. The infrared spectrum of a sixth solution, containing 5.2 μL of MeCN in 0.50 mL of $CHCl_3$, was also taken in this region.

2. ^1H NMR Spectroscopy. $[Pd(PPh_3)_2(MeCN)(COMe)](BF_4)$ (0.0123 g) was dissolved into 1.20 mL of $CDCl_3$, and the resulting solution was divided into two equal portions, which were immediately placed into ^1H NMR tubes. Into one portion were successively added 1.0, 1.0, 3.0, and 28 μL of MeCN, corresponding to 0.3, 0.6, 1.5, and 10 total equiv (relative to palladium), respectively. ^1H NMR spectra were run before and after each addition of MeCN, from which the chemical shifts of the MeCN resonances were determined. The process was repeated for the second portion by successively adding 3.3, 3.3, and 60 μL of MeCN, corresponding in this case to 1.0, 2.0, and 40 total equivalents, respectively.

O. Statistical Analyses of Kinetic Experiments and van't Hoff Plot. A linear regression from a least-squares analysis was performed, from which slopes, intercepts, and correlation coefficients were directly obtained. Errors were calculated at their 95% confidence limits from the appropriate standard deviations and the t-distribution table.

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Registry No. 1a, 20506-42-7; **1b**, 81174-30-3; **1c**, 111771-62-1; **1c***, 111771-63-2; **1d**, 71649-13-3; **1e**, 111771-64-3; **1f**, 111771-65-4; **1g**, 54927-51-4; **1h**, 111771-66-5; **1i**, 111771-67-6; **1j**, 111771-68-7; **1k**, 111771-69-8; **1e**, 111771-70-1; **1m**, 111771-71-2; **1n**, 54927-53-6; **1o**, 50417-59-9; **1o***, 111771-72-3; **2a**, 111771-74-5; **2a***, 111772-11-3; **2b**, 111771-76-7; **2c**, 111771-78-9; **2c***, 111771-80-3; **2d**, 111771-82-5; **2e**, 111771-84-7; **2f**, 111771-86-9; **2g**, 111771-88-1; **2h**, 111771-90-5; **2i**, 111771-92-7; **2j**, 111771-94-9; **2k**, 111771-96-1; **2l**, 111771-98-3; **2m**, 111772-00-0; **2n**, 111772-02-2; **2o**, 111772-04-4; **2o***, 111772-06-6; $Pd(PPh_3)_4$, 14221-01-3; $Pd[P(p\text{-tolyl})_3]_4$, 29032-56-2; $[Pd(PPh_3)(Cl)(CO\text{-}i\text{-}Pr)]_2$, 111772-07-7; $Pd(PhCN)_2Cl_2$, 14220-64-5; $[Pd(PPh_3)(Cl)(COMe)]_2$, 111772-08-8; $[Pd(PPh_3)(Cl)(COEt)]_2$, 111821-50-2; $[Pd(PPh_3)(Cl)(COPh)]_2$, 111821-51-3; $Pd[P(p\text{-tolyl})_3](PPh_3)(Cl)(CO\text{-}i\text{-}Pr)$, 111772-09-9; $[Pd[P(p\text{-tolyl})_3](PPh_3)(MeCN)(COMe)](BF_4)$, 111772-13-5; MeCOCl, 75-36-5; EtCOCl, 79-03-8; *i*-PrCOCl, 79-30-1; *n*-PrCOCl, 141-75-3; *sec*-BuCOCl, 5856-79-1; *n*-BuCOCl, 638-29-9; *t*-BuCOCl, 3282-30-2; *i*-BuCOCl, 108-12-3; $CH_2{=}C(Me)COCl$, 920-46-7; (*E*)-$CH_3C(H)C(H)COCl$, 625-35-4; $Me_2C{=}C(H)COCl$, 3350-78-5; PhCOCl, 98-88-4; $PPh_3(CMe{=}CH_2)^+BF_4^-$, 103730-96-7; $AlCl_3$, 7446-70-0; SnF_4, 7783-62-2; Ph_3P, 603-35-0; (*E*)-$Ph_3P(CH{=}CHMe)^+BF_4^-$, 103730-98-9; $Ph_3P(CH{=}CMe_2)^+BF_4^-$, 111772-16-8; cyclohexylacetylacetyl chloride, 23860-35-7; 1-methylcyclohexanoyl chloride, 2890-61-1; cyclohexanoyl chloride, 2719-27-9; cyclohexene, 110-83-8; ethene, 74-85-1; methylene cyclohexane, 1192-37-6; 1-methyl cyclohexene, 591-49-1; 3-methyl cyclohexene, 591-48-0; 4-methyl cyclohexene, 591-47-9; morpholine, 110-91-8; norbornadiene, 121-46-0; (η^2-oxobutylnorbornene)bis(triphenylphosphine)palladium(1+), 111772-15-7; (η^2-2-methyloxopropylnorbornene)bis(triphenylphosphine)palladium(1+), 111772-14-6.

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