Influence of Ligands and Anions on the Rate of Carbon Monoxide Insertion into Palladium–Methyl Bonds in the Complexes $(P\text{-}P)Pd(CH_3)Cl$ and $[(P\text{-}P)Pd(CH_3)(L)]^+SO_3CF_3^-$ (P-P = dppe, dppp, dppb, dppf; L = CH_3CN, PPh_3)

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The preparation of the neutral complexes $(P\text{-}P)Pd(CH_3)Cl$ (P-P = 1,2-bis(diphenylphosphino)ethane (dppe), 1,3-bis(diphenylphosphino)propane (dppp), 1,4-bis(diphenylphosphino)butane (dppb), 1,1′-bis(diphenylphosphino)ferrocene (dppf)) and the ionic complexes $[(P\text{-}P)Pd(CH_3)(CH_3CN)]^+SO_3CF_3^-$ (P-P = dppe, dppp, dppb, dppf) is described. The ionic dppb complex was formed as a mixture of monomeric and oligomeric forms, which can be attributed to the length and the flexibility of the backbone of the ligand. The rate of CO insertion into the $Pd-CH_3$ bond in these complexes has been studied. The rate was found to decrease in the order dppb ≈ dppp > dppf for the neutral complexes with half-life times ranging from 18 to 36 min at 235 K and 25 bar of CO. The dppe complex reacted much slower with a half-life time of 170 min at 305 K. The rate of carbonylation of the $Pd-CH_3$ bond in the cationic complexes was at least 10 times higher than those of the analogous neutral complexes, the order being dppb ≈ dppp ≈ dppf > dppe with half-life times <1.5 min at 235 K, except for the dppe complex, for which a half-life time of 2.5 min was measured. Carbonylation of the ionic PPh_3-coordinated complex $[(dppp)Pd(CH_3)(PPh_3)]^+SO_3CF_3^-$ was at least 2.5 times slower than that of the analogous CH_3CN-coordinated cationic complex.

Introduction

The mechanism of the carbonylation of metal–alkyl or metal–aryl bonds has been extensively studied for many systems both experimentally[1–4] and theoretically.[5,6] The generally accepted mechanism contains four main features (Figure 1): (i) coordination of a CO molecule to the metal center, (ii) isomerization of the metal–carbonyl complex via pseudorotations to achieve a configuration suitable for alkyl migration, (iii) migration of the alkyl or aryl group to a CO molecule coordinated in a cis position, and (iv) stabilization of the unsaturated complex via association with an additional ligand or η^2-acyl coordination.

Relatively little work has been carried out on the carbonylation of organopalladium compounds. In particular, very few reports have appeared on the carbonylation of methylpalladium complexes containing bidentate ligands with P-P and N-N[7,8] and P-N[9] donor atoms, but the available information shows that the choice of the bidentate ligand has a large influence on the reaction.

Most of the carbonylation studies on the group 10 metals have been concerned with platinum–aryl complexes. The mechanistic results on complexes containing monodentate phosphine ligands[2] are in accord with the above-mentioned scheme. Anderson and Lumetta reported that the rate of carbonylation of the platinum–aryl complexes with bidentate ligands (P-P)Pt(Ph)Cl (P-P = 1,2-bis(diphenylphosphino)ethane (dppe), 1,3-bis(diphenylphosphino)propane (dppp)) was low in both cases, the dppp complex reacting faster.[10] This difference was ascribed to the higher flexibility of the dppp backbone, which gives a lower energy barrier in the dppp complex to conformational rearrangements required for insertion.

When we consider the flexibility of the bidentate ligands dppe, dppp, and 1,4-bis(diphenylphosphino)butane (dppb) coordinated to one metal center, it may be seen that for dppp and dppb the organic backbone is bent out of the plane of coordination and that, in contrast, a skew conformation is observed for dppe.[11] In the dppp and dppb complexes the phenyl groups can bend away from the remaining two coordination sites. Flexible backbones also impose low-energy barriers for the variation of the P–Pd–P angle and Pd–P distances. Moreover, theoretical calculations[5,6] indicate that such flexibility may enhance migration reactions.

Ab initio calculations for the carbonylation of the Pt–CH_3 bond in the model complex $Pt(CH_3)F(CO)(PH_3)$,[12] with CO and CH_3 in relative cis positions, showed that the migration of the methyl group was energetically favored

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(1) (a) Calderazzo, F. *Angew. Chem.* **1977**, *89*, 305. (b) Kuhlmann, E. J.; Alexander, J. J. *Coord. Chem. Rev.* **1980**, *33*, 195. (c) Cardaci, G.; Reichenbach, G.; Bellachioma, G.; Wassink, B.; Baird, M. C. *Organometallics* **1988**, *7*, 2475. (d) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; pp 356–376. (e) Wender, I., Pino, P., Ed.; *Organic Synthesis via Metal Carbonyls*; Wiley: New York, 1977; Vol. 2. (f) Falbe, J., Ed. *New Synthesis with Carbon Monoxide*; Springer-Verlag: New York, 1980.

(2) (a) Anderson, G. K.; Cross, R. J. *Acc. Chem. Res.* **1984**, *17*, 67. (b) Garrou, P. E.; Heck, R. F. *J. Am. Chem. Soc.* **1976**, *98*, 4115.

(3) Noack, K.; Calderazzo, F. *J. Organomet. Chem.* **1967**, *10*, 101.

(4) Ozawa, F.; Yamamoto, A. *Chem. Lett.* **1981**, 289.

(5) Berke, H.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 7224.

(6) (a) Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1985**, *107*, 7230. (b) Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1986**, *108*, 6136. (c) Calhorda, M. J.; Brown, J. M.; Cooley, N. A. *Organometallics* **1991**, *10*, 1431. (d) Koga, N.; Morokuma, K. *Chem. Rev.* **1991**, *91*, 823.

(7) de Graaf, W.; Boersma, J.; Grove, D. M.; Spek, A. L.; van Koten, G. *Recl. Trav. Chim. Pays-Bas* **1988**, *107*, 299.

(8) de Graaf, W.; Boersma, J.; van Koten, G. *Organometallics* **1990**, *9*, 1479.

(9) Dekker, G. P. C. M.; Buijs, A.; Elsevier, C. J.; Vrieze, K.; van Leeuwen, P. W. N. M.; Smeets, W. J. J.; Spek, A. L.; Wang, Y. F.; Stam, C. H. *Organometallics*, in press.

(10) Anderson, G. K.; Lumetta, G. J. *Organometallics* **1985**, *4*, 1542.

(11) Paviglianiti, A. J.; Minn, D. J.; Fultz, W. C.; Burmeister, J. L. *Inorg. Chim. Acta* **1989**, *159*, 65.

(12) Sakaki, S.; Kitaura, K.; Morokuma, K.; Ohkubo, K. *J. Am. Chem. Soc.* **1983**, *105*, 2280.

0276-7333/92/2311-1598$03.00/0

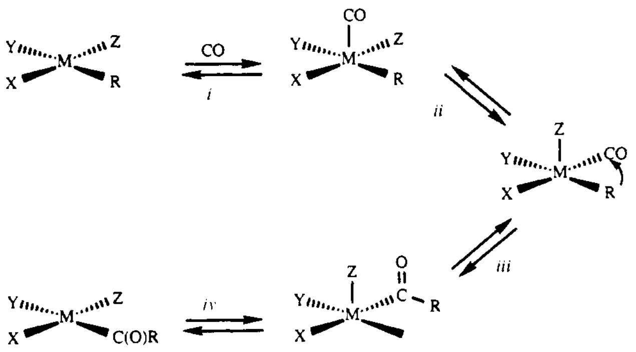


Figure 1. Generally accepted simplified mechanism of CO insertion in M–R bonds in square-planar complexes via addition of CO to the metal center (i), isomerization of the metal–CO intermediate (ii), insertion (iii), and stabilization of the unsaturated product (iv).

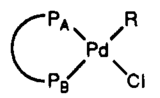
by simultaneous enlargement of the F–Pt–P angle (Figure 2). Hence, when bidentate ligands are used, larger bite angles stabilize the transition state relative to the ground state.

Further, ab initio calculations for carbonylation of the M–R bond in the model complexes $M(R)H(CO)(PH_3)$ (M = Pd, Pt; R = CH_3, CHF_2, CH_2CH_3) showed that the energy of the migration of the methyl group to the carbon monoxide molecule can be lowered in two ways: first, by using ligands with a large trans influence bonded opposite to the migrating alkyl group, and second, by choosing a migrating alkyl group containing electron-releasing substituents.[6a,b] Hence, the migration is best described as a nucleophilic attack of the migrating group at the carbon atom of the coordinated CO molecule.

An important reaction involving CO insertion into metal–alkyl bonds is the copolymerization of CO with alkenes, giving polyketone. Drent has recently reported[13] a catalyst with much lower ligand consumption and higher turnover frequencies than the other published systems.[14] This superior catalyst contains a bidentate phosphine ligand and an ionic Pd salt. We carried out investigations on two important steps of the catalytic cycle, i.e. insertion of carbon monoxide into metal–alkyl bonds and insertion of alkenes into metal–acyl bonds. This paper deals with the CO insertion; the alkene insertion will be described in a separate communication.[15] We focus on the CO insertion in the $Pd-CH_3$ bonds in model complexes for the catalyst system mentioned.[13] Neutral and ionic palladium–methyl complexes $(P-P)Pd(CH_3)Cl$ and $[(P-P)Pd(CH_3)(L)]^+SO_3CF_3^-$ (P-P = dppe, dppp, dppb, 1,1′-bis(diphenylphosphino)ferrocene (dppf); L = CH_3CN, PPh_3) will be studied with particular emphasis on the influence of the phosphine ligands, the anions, and the additional ligands on the rate of insertion. Carbonylation of complexes with P-N ligands has been discussed elsewhere.[9]

Results

Table I. ^1H and $^{31}P\{^1H\}$ NMR and IR Data for Complexes **1a–d** and **2a–d**[a]



compd	^1H NMR for $CH_3/C(O)CH_3$, δ[c] $\{J(P-H)\}$[d]	$^{31}P\{^1H\}$ NMR for P–P,[b] δ[c] $[^2J(P-P)]$[d]	IR $\nu(CO)$[e]
1a	0.64 (dd) {2.9} {8.1}	59.6 (d) [27] 32.0 (d)	
1b	0.62 (dd) {3.7} {7.8}	26.9 (d) [60] –5.8 (d)	
1c	0.69 (dd) {3.9} {7.6}	38.2 (d) [39] 8.8 (d)	
1d	0.79 (dd) {3.7} {7.7}	37.8 (d) [34] 11.9 (d)	
2a	2.05 (t) {1.4} n.o.[f]	38.1 (d) [43] 21.7 (d)	1678
2b	1.93 (t) {1.5} n.o.	12.4 (d) [72] –9.0 (d)	1680
2c	1.77 n.o. n.o.	29.3 (d) [54] –0.7 (d)	1675
2d	1.99 (t) {1.5} n.o.	25.1 (d) [56] 6.6 (d)	1690

[a] In CD_2Cl_2. [b] P_A is the first value and P_B is the second. [c] In ppm. [d] In Hz; $^3J(P-H)$ for 1, $^4J(P-H)$ for 2. [e] In cm^{-1}. [f] n.o. = not observed.

Table II. Reaction Rates ($t_{1/2}$) of the Carbonylation of **1a–d**, **3a–d**, and **5**[a]

compd	T, K	$t_{1/2}$, min[b]	compd	T, K	$t_{1/2}$, min[b]
1a	305	170 ± 5	**3b**	235	<1.5 ± 0.5
1b	235	26 ± 3	**3c**	235	<1.5 ± 0.5
1c	235	18 ± 3	**3d**	235	<1.5 ± 0.5
1d	235	36 ± 4	**5**	235	4 ± 1
3a	235	2.5 ± 0.5			

[a] Conditions: 0.15 mmol in 1.5 mL of CD_2Cl_2, high-pressure NMR tube, 25 bar of CO. [b] Time after which the amounts of starting compound and insertion product were equal.

The neutral complexes $(P-P)Pd(CH_3)Cl$ (**1a–d**; P-P = dppe (**1a**), dppp (**1b**), dppb (**1c**), dppf (**1d**)) were prepared by reaction of $(COD)Pd(CH_3)Cl$[16] with the respective bidentate ligand in benzene (see Experimental Section). The neutral complexes **1a–d** and their carbonylation products $(P-P)Pd(C(O)CH_3)Cl$ (**2a–d**) were characterized by means of ^1H and $^{31}P\{^1H\}$ NMR spectroscopy as well as IR spectroscopy (Table I). Attempts to isolate the acyl complexes were unsuccessful due to gradual decarbonylation upon releasing the CO pressure and working up under an atmosphere of N_2.

From Table I it can be seen that upon carbonylation of the $Pd-CH_3$ bond in complexes **1a–d** all the phosphorus resonances undergo shifts to lower frequencies in the complexes **2a–d** (e.g. from 59.6 and 32.0 in **1a** (dppe) to 38.1 and 21.7 ppm in **2a**). The assignments of P_A and P_B are based on those in analogous platinum complexes, in which the phosphine with the lowest frequency was ascribed to the phosphine trans to the group R.[17,18] Upon carbonylation the phosphine trans to the R group undergoes a smaller shift than the phosphine in a cis position.[17,18] The coupling constants $^2J(P-P)$ increase on going from the methyl complexes **1a–d** to the acetyl complexes **2a–d** (e.g. from 27 to 43 Hz (dppe), from 60 to 72 Hz

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(13) Drent, E. Eur. Pat. Appl. 121,965, 1984.

(14) (a) Gouch, A. Brit. Pat. 081,304, 1967. (b) Fenton, D. M. U.S. Pat. 3,530,109, 1970. (c) Nozaki, K. U.S. Pat. 3,694,412, 1972. (d) Shryne, T. M.; Voller, H. V. U.S. Pat. 3,984,388, 1976. (e) Iwashita, Y.; Sakuraba, M. *Tetrahedron Lett.* **1971**, 2409. (f) Sen, A.; Lai, T.-W. *J. Am. Chem. Soc.* **1982**, *104*, 3520. (g) Sen, A.; Brumbaugh, J. S. *J. Organomet. Chem.* **1985**, *279*, C5. (h) Klabunde, U.; Tulip, T. H.; Roe, D. C.; Ittel, S. D. *J. Organomet. Chem.* **1987**, *334*, 141. (i) Consiglio, G.; Studer, B.; Oldani, F.; Pino, P. *J. Mol. Catal.* **1990**, *58*, L9. (j) Sen, A. *CHEMTECH* **1986**, 48.

(15) Dekker, G. P. C. M.; Elsevier, C. J.; Vrieze, K.; van Leeuwen, P. W. N. M. Submitted for publication in *J. Organomet. Chem.*

(16) (a) van Leeuwen, P. W. N. M.; Roobeek, C. F. Eur. Pat. Appl. 380,162, 1990. (b) Rülke, R. E.; Han, I. M.; Elsevier, C. J.; Vrieze, K.; van Leeuwen, P. W. N. M.; Roobeek, C. F.; Zoutberg, M. C.; Wang, Y. F.; Stam, C. H. *Inorg. Chim. Acta* **1990**, *169*, 5.

(17) Scrivanti, A.; Botteghi, C.; Toniolo, L.; Berton, A. *J. Organomet. Chem.* **1988**, *344*, 261.

(18) Dekker, G. P. C. M.; Elsevier, C. J.; Vrieze, K.; van Leeuwen, P. W. N. M. Unpublished results.

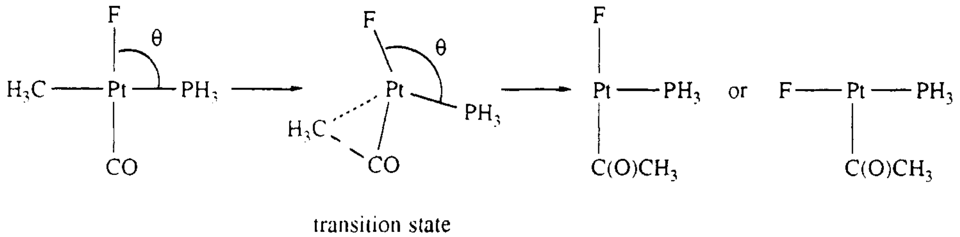


Figure 2. Increase of the angle θ along the reaction path to the transition state in the carbonylation of the Pt–CH_3 bond in the model complex $Pt(CH_3)F(CO)(PH_3)$.[12]

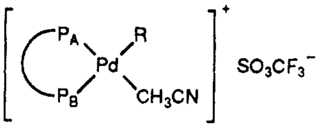
(dppp)). A similar increase in ^2J(P–P) was reported for the carbonylation products of *cis*-$Pt(SnCl_3)(Et)$(P-P) (P-P = dppp, dppb).[17]

The rate of reaction of **1a–d** with CO was studied by using a high-pressure NMR tube,[19a] employing samples of the Pd–CH_3 complex **1a–d** with concentrations of approximately 0.1 M in CD_2Cl_2 at 235 K at a pressure of 25 bar (complete conversion of the complex used corresponds to a pressure drop of less than 2.0 bar). The rates are reported as half-life times; the half-life times were obtained from the decay and increase of the Pd–CH_3 and Pd–C(O)CH_3 ^1H and $^{31}P\{^1H\}$ NMR signals of **1a–d** and **2a–d**, respectively. The time at which the intensities of these signals were equal was taken as the half-life time (Table II).

Complex **1a** showed no insertion of CO in the Pd–CH_3 bond at 235 K. Heating of the reaction mixture up to 305 K resulted in a measurable carbonylation rate, albeit still low compared with the rates observed for **1b–d** at 235 K (Table II). The complexes **1b,c** showed similar half-life times (18–26 min), while for **1d** a slightly longer time (36 min) was observed (Table II).

When the CO pressure was released and N_2 was added, the complexes decarbonylated slowly on standing, while decomposition to Pd(0) and unidentified species took place as well. The ionic complexes $[(P\text{-}P)Pd(CH_3)(CH_3CN)]^+SO_3CF_3^-$ (**3a–d**; P-P = dppe (**3a**), dppp (**3b**), dppb (**3c**), dppf (**3d**)) were prepared in CH_2Cl_2 by reaction of the neutral complexes **1a–d** with $AgSO_3CF_3$ in the presence of 1 equiv of CH_3CN (see Experimental Section). Complexes **3a,b,d** and their carbonylation products[19b] $[(P\text{-}P)Pd(C(O)CH_3)(CH_3CN)]^+SO_3CF_3^-$ (**4a,b,d**) (Table III) were characterized by $^{31}P\{^1H\}$ and ^1H NMR and IR spectroscopy. The reaction of **3a,b,d** with CO was studied under the same circumstances applied for the reaction of **1a,b,d** with CO. Upon carbonylation of the Pd–CH_3 complexes **3a,b,d** the phosphorus resonances shift to lower frequencies (e.g. from 60.4/35.2 to 38.4/23.7 ppm (dppe) and from 27.0/–3.7 to 10.1/–4.9 ppm (dppp)). An increase in value of the coupling constants ^2J(P–P) was observed from 27 (**3a**) to 44 Hz (**4a**) for the dppe complexes, from 54 to 80 Hz (dppp), and from 34 Hz to 56 Hz (dppf) (Table III). It should be noted that carbonylation of complex **3d** gave the insertion product **4d** together with unidentified products of low intensity in the $^{31}P\{^1H\}$ NMR spectrum.

Table III. ^1H and $^{31}P\{^1H\}$ NMR and IR Data for Complexes 3a–d and 4a–d[a]



compd	^1H NMR for CH_3/C(O)CH_3, δ[c] {J(P–H)}[d]	$^{31}P\{^1H\}$ NMR for P–P,[b] δ[c] [^2J(P–P)][d]	IR ν(CO)[e]
3a	0.69 (dd) {2.0} {7.6}	60.4 (d) [27] 35.2 (d)	
3b	0.35 {2.5} {7.4}	27.0 (d) [54] –3.7 (d)	
3c	0.65[f] {2.2} {6.9}	34.7 (d) [41] 16.4 (d)	
	0.16[g] {7}	22.6 (s)	
	0.17[g] {7}	22.2 (s)	
3d	0.71 {3.3} {7.1}	39.6 (d) [34] 15.9 (d)	
4a	2.03 (s) n.o.[i] n.o.	38.4 (d) [44] 23.7 (d)	1690
4b	1.89 (s) {0.9} n.o.	10.1 (d) [80] –4.9 (d)	1690
4c[h]	1.50 (s) n.o. n.o. 1.42 (s) n.o. n.o.	13.6 (s) 13.3 (s)	1690–1710
4d	2.01 (s) n.o. n.o.	23.2 (d) [56] 4.5 (d)	1710

[a] In CD_2Cl_2. [b] P_A is the first value and P_B is the second. [c] In ppm. [d] In Hz; ^3J(P–H) for **3**, ^4J(P–H) for **4**. [e] In cm^{-1}. [f] Monomeric complex. [g] Two triplets due to two oligomeric complexes. [h] Only two oligomeric complexes observed. [i] n.o. = not observed.

The coordination behavior of dppb is somewhat more complicated. In addition to the expected pair of doublets at 34.7 and 16.4 ppm (^2J(P-P) = 41 Hz), the $^{31}P\{^1H\}$ NMR spectrum of complex **3c** also showed two singlets at 22.6 and 22.2 ppm. In the ^1H NMR spectrum three methyl signals are observed. One, which is present in about 50% of the total amount of **3c**, appears at 0.65 ppm as a double doublet with coupling constants $^3J(P\text{–}H)_{cis}$ = 2.2 Hz and $^3J(P\text{–}H)_{trans}$ = 6.9 Hz. This signal, together with the pair of doublets in the $^{31}P\{^1H\}$ NMR spectrum, is assigned to $[(dppb)Pd(CH_3)(CH_3CN)]^+SO_3CF_3^-$, similar to **1c**. The other two methyl resonances in the ^1H NMR spectrum, each 25% in intensity of the total amount of **3c**, appear as triplets at significantly lower frequency, i.e. 0.16 and 0.17 ppm, with coupling constants ^3J(P–H) = 7 Hz (Table III). It has been reported for *trans*-$(PPh_3)_2Pd(CH_3)I$ that the methyl resonance occurs at 0.18 ppm (^3J(P–H) = 5 Hz).[20] These data and those found for **3c**, i.e. two singlets in the $^{31}P\{^1H\}$ NMR spectrum and two triplets in the ^1H NMR spectrum, strongly point to two trans-phosphorus complexes for **3c**. We suggest that in addition to $[(dppb)Pd(CH_3)(CH_3CN)]^+SO_3CF_3^-$ oligomeric species $[(dppb)Pd(CH_3)(CH_3CN)]_n^{n+}(SO_3CF_3^-)_n$ ($n \geq 2$) are also present (Figure 3). In these oligomers the dppb ligands are bridging between the Pd centers, which is a well-known propensity of the dppb ligand[17,21] and other ligands forming seven-membered rings on monometallic complexation.[22]

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[19] (a) Roe, D. C. *J. Magn. Reson.* **1985**, *63*, 388. (b) Very recently the closely related complex $[(dppe)Pd(C(O)CH_3)(CH_3CN)]^+BF_4^-$ has been reported.[19c] (c) Ozawa, F.; Hayashi, T.; Koide, H.; Yamamoto, A. *J. Chem. Soc., Chem. Commun.* **1991**, 1469.

[20] Fitton, P.; Johnson, M. P.; McKeon, J. E. *Chem. Commun.* **1968**, 6.

[21] Sanger, A. R. *J. Chem. Soc., Dalton Trans.* **1979**, 1971.

[22] de Graaf, W.; Boersma, J.; van Koten, G.; Elsevier, C. J. *J. Organomet. Chem.* **1989**, *378*, 115.

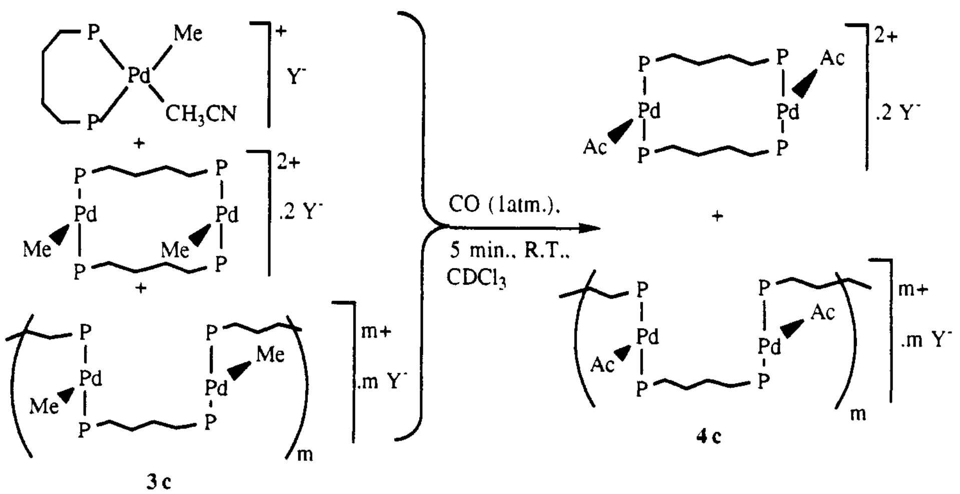
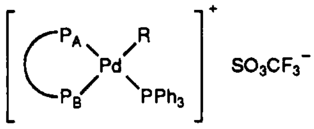


Figure 3. Carbonylation of the Pd–CH$_3$ bond in the monomeric [(dppb)Pd(CH$_3$)(CH$_3$CN)]$^+$SO$_3$CF$_3$$^-$ and oligomeric [(dppb)Pd(CH$_3$)(CH$_3$CN)]$_n$$^{n+}$(SO$_3CF_3$$^-$)$_n$ ($n \geq 2$) complexes (**3c**) to form the oligomeric palladium-acyl complexes [(dppb)Pd(C(O)CH$_3$)(CH$_3$CN)]$_n$$^{n+}$(SO$_3CF_3$$^-$)$_n$ ($n \geq 2$) (**4c**) (Y$^-$ = SO$_3$CF$_3$$^-$; Me = CH$_3$; Ac = C(O)CH$_3$; $m = n - 1$).

Table IV. Relevant ^{31}P{^{1}H} and ^{1}H NMR Data for Complexes 5 and 6



compd	δ(P$_A$)	δ(P$_B$)	δ(P$_C$)	^2J(P$_A$–P$_B$), Hz	^2J(P$_A$–P$_C$), Hz	^2J(P$_B$–P$_C$), Hz	δ(R) (^{1}H)
5[a] (R = CH$_3$)	13.2	−2.3	34.9	55	−361	36	0.24[b]
6[a,c] (R = C(O)CH$_3$)	−7.2	−4.9	20.3	65	−230	47	1.41[d]

[a] In CD$_2$Cl$_2$. [b] Coupling constants ^3J(P–H) = 13.1 and 6.3 Hz. [c] Coupling constants obtained via simulation of the spectrum (see Experimental Section). [d] Coupling constant ^4J(P–H) = 1.3 Hz.

The CO insertion product **4c** only shows two singlets at 13.6 and 13.3 ppm in the ^{31}P{^{1}H} NMR spectrum. The ^{1}H NMR spectrum shows acyl resonances at 1.42 and 1.50 ppm, while no coupling constants ^4J(P–H) are observed. For *trans*-(PPh$_3$)$_2$Pd(C(O)CH$_3$)Cl a methyl resonance at 1.4 ppm has been reported, no coupling constant ^4J(P–H) being observed.[20] On the basis of the analogy of the data found for **4c** with those of the proposed oligomeric complexes of **3c**, we suggest that **4c** also occurs as the oligomeric species [(dppb)Pd(C(O)CH$_3$)(CH$_3$CN)]$_n$$^{n+}$(SO$_3CF_3$$^-$)$_n$ ($n \geq 2$) (Figure 3). The complete formation of the trans-phosphine complexes for **4c** and only the partial formation of these complexes for **3c** is ascribed to the larger trans influence of the acyl group as compared with that of the methyl group.[23] Due to the large trans influence of the organic group the trans-phosphine complexes are thermodynamically more stable than the cis-phosphine complex. The formation of oligomeric species for the ionic complexes **3c** and **4c** and the absence of such species for the neutral complexes **1c** and **2c** imply that the combination of a very weak ligand and a σ-carbon ligand with a large trans influence favors energetically a trans configuration of the phosphines.

Attempts to isolate the palladium–acyl complexes **4a–d** failed due to smooth decarbonylation of these complexes when the CO pressure was released. The half-life times of the rates of carbonylation for complexes **3b–d** were too short to be measured under the circumstances applied (see Table II and Experimental Section); we could only discriminate between the rates of **3a** and **3b–d** (Table II). Lowering the temperature to about 220 K resulted in broadening of the signals in both ^{1}H and ^{31}P{^{1}H} NMR spectra, which prevented the determination of the half-life times.

Table V. Angles P–Pd–P (deg) in the Complexes (P–P)Pd(X)(Y)

P–P	X = Y = *N*CS	X = *S*CN, Y = *N*CS	X = Y = Cl
dppe		85.1 (1)[24]	85.82 (7)[25]
dppp	89.23 (3)[24]	89.0 (1)[11]	90.58 (5)[25]
dppb		92.8 (1);[11] 92.9 (1)[11]	
dppf			99.07 (5)[26]

The complex [(dppp)Pd(CH$_3$)(PPh$_3$)]$^+$SO$_3$CF$_3$$^-$ (**5**) was prepared from **1b**, silver triflate, and PPh$_3$ (for ^{1}H NMR and ^{31}P{^{1}H} NMR data, see Table IV). This complex was made to react with CO under the standard conditions to give **6**, [(dppp)Pd(C(O)CH$_3$)(PPh$_3$)]$^+$SO$_3$CF$_3$$^-$ (for NMR data see Table IV). The rate of carbonylation of **5** (under the same conditions as applied for **1b** and **3b**, 25 bar and 235 K) was between the rates found for **1b** and **3b** (Table II); the half-life time (min) was 4 ± 1 for **5** against 26 ± 3 for **1b** and <1.5 ± 0.5 for **3b**.

Discussion

Influence of the Ligand P-P on the Rate of Carbonylation for (P-P)Pd(CH$_3$)Y Complexes 1a–d, 3a–d, and 5. Carbonylation of the Pd–CH$_3$ bond in the complexes **1a–d** and **3a–d** shows a rate that decreases in the order dppb (**c**) ≥ dppp (**b**) ≥ dppf (**d**) ≫ dppe (**a**). Apparently, structural data are a key factor in determining the reactivities of the complexes, but unfortunately no crystal data are available for complexes **1a–d** and **3a–d**. Therefore, we will summarize the structural data of a few related palladium complexes of dppe, dppp, dppb, and dppf complexes as found in the literature (Table V).

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(23) Dent, S. P.; Eaborn, C.; Pidcock, A.; Ratcliff, B. *J. Organomet. Chem.* **1972**, *46*, C68.

The P–Pd–P angle for dppe complexes ranges from 85.1 (1)° for (dppe)Pd(NCS)(SCN)[24] to 85.82 (7)° for (dppe)PdCl$_2$.[25] In dppp complexes this angle ranges from 89.0 (1)° for (dppp)Pd(NCS)(SCN)[24] to 90.58 (5)° for (dppp)PdCl$_2$,[25] while an angle of 89.32 (3)° was observed in (dppp)Pd(NCS)$_2$.[24] In (dppb)Pd(NCS)(SCN) the P–Pd–P angle is approximately 92.9°,[11] and in (dppf)PdCl$_2$ the angle is 99.07 (5)°.[26] Via nonbonding interactions, a large P–Pd–P angle in the ground state of complexes (P-P)Pd(CH$_3$)Y will induce a small CH$_3$–Pd–Y angle. In the carbonylation process (Y^- = CO), a large P–Pd–P angle pushes the methyl group in the ground state toward the CO molecule, and intuitively one would conclude that ligand repulsions will bring the ground state closer to the transition state, both sterically and energetically. So far, a theoretical corroboration including steric effects is lacking.

Semiempirical calculations[5] by Berke and Hoffmann indicated that bonding interactions resulting from a large P–Pd–P angle also lead to a rate-enhancing effect. They concluded, therefore, that square-planar complexes with bidentate ligands such as dppe should be less prone to migration reactions than monodentate phosphine complexes (vide infra). Ab initio calculations by Sakaki et al.[12] (Figure 2) showed that an increase of the F–Pt–P angle in Pt(CH$_3$)F(CO)(PH$_3$) during the migration process lowers the activation energy. This means that flexible ligands facilitate the insertion process and increase the rate. The present results confirm the predictions based on the theoretical calculations. The ligands dppb, dppp, and dppf have a much more flexible backbone and a larger bite angle than dppe (see Introduction), and hence, the migration will take place more readily for the complexes containing dppp, dppb, and dppf than for the dppe complex.

In addition to its effect on the migration, the flexibility will also facilitate the pseudorotations within the five-coordinate intermediates that may be involved in the carbonylation mechanism (Figure 1). This is of particular importance for complexes in which exchange of the ligands with CO would take place via an associative process. Of the present complexes those with Cl$^-$ might be involved in associative exchange reactions.[18] The extremely large difference in the chloride series **1a–d** between the dppe complex on the one hand and the dppp, dppb, and dppf complexes on the other hand may well be caused in part by the difference of the rates of ligand-exchange reactions.

A complicating factor is that larger numbers of carbon atoms ($n > 3$) in the bridging backbone connecting the two phosphine atoms promote formation of oligomeric complexes, as was illustrated for the ionic dppb complex **3c**. About half of the complex occurs in a trans configuration. For the trans complex a decrease of the rate of carbonylation would be expected, since there is neither a CO in a position cis to the methyl group, as would be required for a cis-migration process, nor is there a phosphine trans to the Pd–CH$_3$ bond that can activate the migrating methyl group. The rate of carbonylation of **3c** was still high and could not be distinguished from the rates found for the dppp and dppf complexes, thus proving that rearrangements are fast with respect to carbonylation.

Comparison of the order of the rate of carbonylation (dppb ≥ dppp ≥ dppf ≫ dppe) with the order of decreasing P–Pd–P angles (dppf > dppb > dppp > dppe) shows that dppf is an exception if one only considers the bite angle and the flexibility of the backbone. The dppf ligand is more flexible than is indicated by the bite angle in (dppf)PdCl$_2$ since it even forms complexes with the two phosphines trans to one another.[27] However, these are not the only factors that should be taken into account; dppf has a cyclopentadienyl unit attached to the phosphorus atom, whereas dppe, dppp, and dppb have an alkyl group instead and electronic influences might also play a role.

Influence of Anions and/or Ligands on the Rate of Carbonylation for (P-P)Pd(CH$_3$)Cl and [(P-P)Pd(CH$_3$)(L)]$^+$Y$^-$ Complexes 1a–d, 3a–d, and 5. Carbonylation of the Pd–CH$_3$ bond in the ionic complexes **3a–d** and **5** proceeded much faster than in the neutral complexes **1a–d**. The ease of replacement of the coordinating anion and/or neutral ligand by CO increases in the order Cl$^-$ < PPh$_3$ < CH$_3$CN.[28] The order found for the increasing rate of carbonylation of the Pd–CH$_3$ bond in complexes **1**, **3**, and **5**, i.e. **1** < **5** < **3**, is the same as the order for the strength of coordination of the anion and/or neutral ligand, which means that the rate is largely dependent on the accessibility of a coordination site at the Pd center. The importance of the accessibility of a coordination site was already shown by Kubota et al. for the platinum complex (PPh$_3$)$_2$Pt(C(O)R)Cl (R = Me, Ph, *p*-MeC$_6$H$_4$, *p*-MeOC$_6$H$_4$, *p*-O$_2$NC$_6$H$_4$).[29] Upon abstraction of Cl$^-$ by addition of AgPF$_6$, the formed ionic complex [(PPh$_3$)$_2$Pt(C(O)R)]$^+$PF$_6^-$ decarbonylated easily, yielding the Pt–CO complex [(PPh$_3$)$_2$Pt(R)CO]$^+$PF$_6^-$, whereas decarbonylation of the neutral complex (PPh$_3$)$_2$Pt(C(O)R)Cl only took place when the complex was heated to 210 °C.[29] When the abstraction of the Cl$^-$ anion was performed in CH$_3$CN, no decarbonylation took place due to blocking of the vacant coordination site by the solvent.

Conclusions

Within the series of neutral complexes (P-P)Pd(CH$_3$)Cl or ionic complexes [(P-P)Pd(CH$_3$)(L)]$^+$SO$_3$CF$_3^-$, the rate of carbon monoxide insertion in the palladium–methyl bond depends mainly on the flexibility of the backbone of the ligand, which is in accord with theoretical calculations. The use of a strongly coordinating ligand lowers the rate of carbonylation of the Pd–CH$_3$ bond of the cationic complexes.

Our studies have clearly shown that the bite angle and backbone flexibility of the ligand strongly influence the rate of migration in methyl–palladium complexes, and the question arises whether this will affect catalytic processes in a similar manner. There are several examples which seem to point to a rate-enhancing effect obtained by replacing the two-carbon bridge by a three- or four-carbon bridge in 1,*n*-bis(diphenylphosphino)alkanes: (a) the palladium-catalyzed copolymerization of CO and ethene,[13] (b) the platinum-catalyzed hydroformylation of alkenes,[30]

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(24) Palenik, G. J.; Matthew, M.; Steffen, W. L.; Beran, G. *J. Am. Chem. Soc.* **1975**, *97*, 1059.

(25) Steffen, W. L.; Palenik, G. J. *Inorg. Chem.* **1976**, *15*, 2432.

(26) Hayashi, T.; Konishi, M.; Kobori, Y.; Kumada, M.; Higuchi, T.; Hirotsu, K. *J. Am. Chem. Soc.* **1984**, *106*, 158.

(27) (a) Sato, M.; Sekino, M.; Akabori, S. *J. Organomet. Chem.* **1988**, *344*, C31. (b) Recently Whiteker and Casey[27c,d] introduced the concept of "natural bite angle" of bidentate ligands as being the angle corresponding to the energy minimum obtained in a molecular mechanics calculation which includes only backbone constraints and ignores metal valence angles. It would be interesting to see the behavior of dppf in such a calculation. (c) Casey, C. P.; Whiteker, G. T. *J. Org. Chem.* **1990**, *55*, 1394. (d) Casey, C. P.; Whiteker, G. T. *Isr. J. Chem.* **1990**, *30*, 299.

(28) Davies, J. A.; Hartley, F. R.; Murray, S. G. *Inorg. Chem.* **1980**, *19*, 2299.

(29) Kubota, M.; Rothrock, R. K.; Geibel, J. *J. Chem. Soc., Dalton Trans.* **1973**, 1267.

(30) (a) Kawabata, Y.; Hayashi, T.; Ogata, I. *J. Chem. Soc., Chem. Commun.* **1979**, 462. (b) Kawabata, Y.; Hayashi, T.; Isoyama, T.; Ogata, I. *Bull. Chem. Soc. Jpn.* 1981, *54*, 3438.

(c) the palladium-catalyzed methoxycarbonylation of styrene[31] and (d) alkyl to vinyl migration in a palladium-catalyzed carbon–carbon bond formation.[6c,32] Even if we assume that alkene insertions are similarly affected in catalytic processes, the migration reactions constitute only part of a catalytic cycle and, therefore, the present rate-enhancing effect may not always be reflected in the overally reaction rate.

Experimental Section

All reactions and manipulations were carried out under purified nitrogen using Schlenk techniques. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AC 100 spectrometer at 100.13 and 40.53 MHz, respectively. Shifts are relative to $(CH_3)_4Si$ (^1H) and 85% H_3PO_4 (^{31}P) as external standards, where positive shifts are to high frequency. Simulations of the spectra were carried out at the Koninklijke/Shell-Laboratorium Amsterdam with the program geNMR, version 3.1 (IvorySoft, Amsterdam, 1989). IR spectra were recorded with a Perkin-Elmer 283 spectrometer. CH_2Cl_2 and CH_3CN were dried over P_2O_5. Benzene, diethyl ether, and pentane were dried over Na wire. All solvents were distilled from the respective desiccants and stored under nitrogen. (COD)Pd(CH_3)Cl was prepared according to published methods.[16] Dppe, dppp, dppb, and dppf were obtained from Strem Chemicals and were used without purification. PPh_3 and $Sn(CH_3)_4$ were obtained from Merck. Silver trifluoromethanesulfonate ($AgSO_3CF_3$) was obtained from Janssen Chimica. Ultra High Purity CO gas (NMR experiments) and CP-grade CO gas (synthetic experiments) were both obtained from Matheson.

(dppe)Pd(CH_3)Cl (1a). To a solution of (COD)Pd(CH_3)Cl (0.82 g, 3.1 mmol) in benzene (15 mL) was added a solution of 1 equiv of dppe (1.23 g, 3.1 mmol) in benzene (10 mL). After the mixture was stirred for 1 h, the white product was filtered off and washed with benzene (2 × 5 mL) and pentane (2 × 5 mL). The product was recrystallized from a CH_2Cl_2/diethyl ether mixture. The yield was 1.43 g (83%) of a white powder. Anal. Calcd for $C_{27}H_{27}P_2ClPd$: C, 58.40; H, 4.90; P, 11.15. Found: C, 57.83; H, 5.01; P, 10.55.

(dppp)Pd(CH_3)Cl (1b), (dppb)Pd(CH_3)Cl (1c), and (dppf)Pd(CH_3)Cl (1d). The same procedure was used as for the preparation of **1a** except that dppp, dppb, and dppf were used instead of dppe. Yield: 94% of a white powder (**1b**), 57% of a white powder (**1c**), 85% of an orange-brown powder (**1d**). Anal. Calcd for $C_{28}H_{29}P_2ClPd$ (**1b**): C, 59.07; H, 5.14; P, 10.88. Found: C, 58.41; H, 4.90; P, 10.86. Calcd for $C_{29}H_{31}P_2ClPd$ (**1c**): C, 59.71; H, 5.36; P, 10.62. Found: C, 59.64; H, 5.44; P, 10.54. Calcd for $C_{35}H_{31}P_2ClFePd$ (**1d**): C, 59.10; H, 4.39; P, 8.71. Found: C, 59.78; H, 4.17; P, 8.54.

(dppp)Pd(C(O)CH_3)Cl (2b). A gentle stream of CO (ca. 40 mL/min) was passed through a solution of approximately 40 mg of **1b** in 0.5 mL of CD_2Cl_2 in a 5-mm NMR tube over $^3/_4$ h. Attempts to isolate the product were unsuccessful due to decarbonylation upon releasing the CO pressure and adding N_2.

(dppe)Pd(C(O)CH_3)Cl (2a), (dppb)Pd(C(O)CH_3)Cl (2c), and (dppf)Pd(C(O)CH_3)Cl (2d). These complexes were prepared in a way similar to that used for the preparation of **2b**.

[(dppe)Pd$(CH_3)(CH_3CN)]^+SO_3CF_3^-$ (3a). To a rapidly stirred solution of **1a** (0.28 g, 0.50 mmol) in 15 mL of CH_2Cl_2/CH_3CN (14:1, v/v) was added dropwise a solution of $AgSO_3CF_3$ (0.13 g, 0.50 mmol) in 2 mL of CH_3CN. The immediately formed white suspension was filtered off to remove AgCl, and the filtrate was collected in 30 mL of cooled (−20 °C) diethyl ether with rapid stirring. Purification was similar to that for **1a**. The yield was 0.29 g (82%) of a white powder. Anal. Calcd for $C_{30}H_{30}P_2NO_3SF_3Pd$: C, 50.75; H, 4.26; P, 8.72. Found: C, 50.11; H, 4.34; P, 8.51.

[(dppp)Pd$(CH_3)(CH_3CN)]^+SO_3CF_3^-$ (3b), [(dppb)Pd$(CH_3)(CH_3CN)]^+SO_3CF_3^-$ (3c), and [(dppf)Pd$(CH_3)(CH_3CN)]^+SO_3CF_3^-$ (3d). The same procedure was used as for the preparation of **3a** except that dppp, dppb, and dppf were used instead of dppe. Yield: 84% of a white powder (**3b**), 88% of a white powder (**3c**), 79% of an orange-brown powder (**3d**). Anal. Calcd for $C_{31}H_{32}P_2NO_3SF_3Pd$ (**3b**): C, 51.43; H, 4.46; P, 8.56. Found: C, 51.36; H, 4.53; P, 8.48. Calcd for $C_{32}H_{34}P_2NO_3SF_3Pd$ (**3c**): C, 52.08; H, 4.64; P, 8.39. Found: C, 51.44; H, 4.60; P, 8.43. Calcd for $C_{38}H_{34}P_2NO_3SF_3FePd$ (**3d**): C, 52.17; H, 3.96; P, 7.15. Found: C, 52.58; H, 4.07; P, 7.08.

[(dppe)Pd(C(O)$CH_3)(CH_3CN)]^+SO_3CF_3^-$ (4a), [(dppp)Pd(C(O)$CH_3)(CH_3CN)]^+SO_3CF_3^-$ (4b), [(dppb)Pd(C(O)$CH_3)(CH_3CN)]^+SO_3CF_3^-$ (4c), and [(dppf)Pd(C(O)$CH_3)(CH_3CN)]^+SO_3CF_3^-$ (4d). These complexes were prepared analogously to the preparation of **2b**.

[(dppp)Pd$(CH_3)(PPh_3)]^+SO_3CF_3^-$ (5). To a solution of **1b** (0.53 g, 0.93 mmol) in CH_2Cl_2 (5 mL) was added 1 equiv of $AgSO_3CF_3$ (0.23 g, 0.93 mmol). After the mixture was stirred for 5 min 1 equiv of PPh_3 (0.24 g, 0.93 mmol) was added. Filtration followed by evaporation of the solvent afforded the product, which was washed with diethyl ether (3 × 5 mL) and pentane (2 × 5 mL) and dried under vacuum. Yield: 0.67 g (76%) of pale yellow powder. Anal. Calcd for $C_{47}H_{44}P_3O_3SF_3Pd$ (**5**): C, 59.72; H, 4.70; P, 9.83. Found: C, 59.53; H, 4.34; P, 9.28.

[(dppp)Pd(C(O)$CH_3)(PPh_3)]^+SO_3CF_3^-$ (6). This compound was prepared by a procedure analogous to the preparation of **2b**.

Carbonylation of the Pd–CH_3 Bond in Complexes 1a–d, 3a–d, and 5 (NMR High-Pressure Experiments). The complexes were dissolved in CD_2Cl_2 (0.15 mmol in 1.5 mL) and were, under a nitrogen atmosphere, transferred into the high-pressure NMR tube. The NMR tube was cooled to approximately 200 K, and subsequently a pressure of 25 bar of CO was applied. The tube was shaken five times and transferred to the NMR spectrometer. After 3 min the first spectrum could be obtained. During the reaction the tube was shaken after 30 min and after 60 min.

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Registry No. **1a**, 64406-71-9; **1b**, 139168-06-2; **1c**, 139168-07-3; **1d**, 139198-75-7; **2a**, 139168-08-4; **2b**, 139168-09-5; **2c**, 139168-10-8; **2d**, 139168-11-9; **3a**, 139168-12-0; **3b**, 139168-14-2; **3c**, 139168-16-4; **3d**, 139168-18-6; **4a**, 139168-19-7; **4b**, 139168-21-1; **4c**, 139168-23-3; **4d**, 139198-77-9; **5**, 139168-25-5; **6**, 139168-27-7; dppe, 1663-45-2; dppp, 6737-42-4; dppb, 7688-25-7; dppf, 12150-46-8; (COD)Pd(CH_3)Cl, 64946-85-6; [(dppb)Pd$(CH_3)(CH_3CN)]_n^{n+}(SO_3CF_3^-)_n$, 139168-29-9.

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[31] Sugi, Y.; Bando, K. *Chem. Lett.* **1976**, 727.

[32] Yamamura, M.; Moritani, I.; Murahashi, S. I. *Chem. Lett.* **1974**, 1423.