

Journal of Organometallic Chemistry, 405 (1991) 133–140
Elsevier Sequoia S.A., Lausanne
JOM 21416

Novel ketene formation by reactions of acid chlorides with low-valent platinum complexes

Youichi Ishii, Yoshihiro Kobayashi, Masakazu Iwasaki and Masanobu Hidai *

Department of Synthetic Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113 (Japan)

(Received August 9th, 1990)

Abstract

$\text{Pt}(\text{CO})_n(\text{PPh}_3)_{4-n}$ ($n = 0-2$) reacts with Ph_2CHCOCl under CO to afford diphenylketene and *trans*- $\text{PtHCl}(\text{PPh}_3)_2$. For this reaction, the rate law is zero order in the platinum complex, first order in Ph_2CHCOCl , and first order in free PPh_3 . A primary isotope effect ($k_{\text{H}}/k_{\text{D}} = 4.5$) was observed in the reaction of Ph_2CDCOCl . A mechanism is proposed which involves the rate-determining enolization of Ph_2CHCOCl by PPh_3 followed by fast abstraction of HCl by a platinum(0) complex.

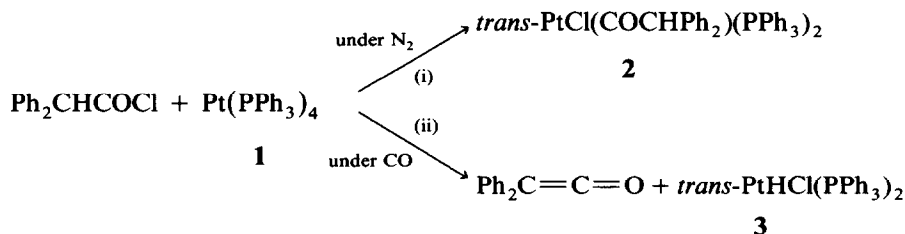
Introduction

Ketenes and ketene complexes have received increasingly more attention as important intermediates in transition metal-promoted reactions such as CO hydrogenation [1] and carbonylation of organic or organometallic compounds [2]. A variety of transition metal-ketene complexes have been reported [3]. Although it is well-known that ketenes can be prepared by treatment of acid halides with bases such as tertiary amines [4], reactions of low-valent metal complexes with acid halides usually result in the formation of metal acyl complexes instead of ketenes in spite of their basic character. Only a few ruthenium complexes have been reported to give ketenes when treated with acid chlorides [5,6]. However, the reaction mechanism of this dehydrohalogenation has been ambiguous, although a cationic acylruthenium complex has been proposed as an intermediate.

We recently developed a novel palladium- or platinum-catalyzed cyclocarbonylation of cinnamyl compounds which yields fused aromatic compounds [7,8]. A possible mechanism of this reaction involves a vinyl ketene intermediate [8]. We have therefore embarked on an investigation of ketene formation in the presence of palladium and platinum complexes. Here we describe the novel formation of diphenylketene by reaction of platinum(0) complexes with diphenylacetyl chloride.

Results and discussion

When an excess amount of Ph_2CHCOCl was allowed to react with $\text{Pt}(\text{PPh}_3)_4$ (1), under N_2 in benzene or toluene at r.t., the usual oxidative addition occurred to give



Scheme 1

a colorless acyl complex *trans*-PtCl(COCHPh₂)(PPh₃)₂ (**2**) [9]. In contrast, when a similar reaction was conducted under CO, the color of the solution gradually turned the characteristic yellow of diphenylketene. Formation of diphenylketene was confirmed from the strong absorption at 2100 cm⁻¹ [4] in the IR spectrum of the solution. However, no absorption due to **2** was observed. The yield of diphenylketene determined by the absorbance at 2100 cm⁻¹ reached 88% based on **1**, although it could not be isolated because of its instability. Addition of hexane to the reaction mixture afforded *trans*-PtHCl(PPh₃)₂ (**3**) in 89%. This result indicates that only under CO the reaction path ii proceeds and the usual oxidative addition path i is completely suppressed (Scheme 1).

This type of ketene formation was found to depend largely on the acid chloride used. Phenylacetyl chloride was also found to react with **1** under CO at r.t. to give **3** (68%) and the IR spectrum of the reaction mixture exhibited absorptions at 1905, 1878, and 1710 cm⁻¹ indicating the formation of phenylketene dimer [10]. Other acid chlorides such as acetyl chloride, isobutyryl chloride, 2-phenylpropionyl chloride did not react with **1** under CO at r.t., although these chlorides gave the corresponding acyl complexes under N₂. A similar reaction of Ph₂CHCOCl with Pt[P(OPh)₃]₄ also produced diphenylketene, but the reaction was very sluggish and therefore not investigated in detail. It should be mentioned that the ketene formation does not proceed with palladium complexes. Thus, the reactions of Ph₂CHCOCl under CO with Pd(PPh₃)₄ or Pd(CO)(PPh₃)₃ gave only *trans*-PdCl(COCHPh₂)(PPh₃)₂, and no diphenylketene was detected by IR.

Since **1** is known to establish an equilibrium with Pt(CO)(PPh₃)₃ (**4**) and Pt(CO)₂(PPh₃)₂ (**5**) under CO (Scheme 2) [11], reactions of excess Ph₂CHCOCl with **1**, **4**, and **5** were monitored by measuring the IR absorption at 2100 cm⁻¹ at different times. As can be seen from Fig. 1, the amount of diphenylketene increased linearly with the reaction time, which suggests that the reaction rate is zero order with respect to the platinum complex concentration. The reaction rates were found to fall in the order **1** > **4** > **5**. In view of this fact, PPh₃, dissociated from the platinum complexes, seems to accelerate the reaction, although no reaction was observed by either ¹H NMR or IR when Ph₂CHCOCl was allowed to stand in contact with PPh₃ in benzene under CO.

In order to elucidate the mechanism of this ketene formation, the kinetics of the reaction were studied at 29°C in benzene. When the initial concentration of **1** was fixed, the initial rate was proportional to the initial concentration of Ph₂CHCOCl (Fig. 2). On the other hand, when the initial concentration of Ph₂CHCOCl was

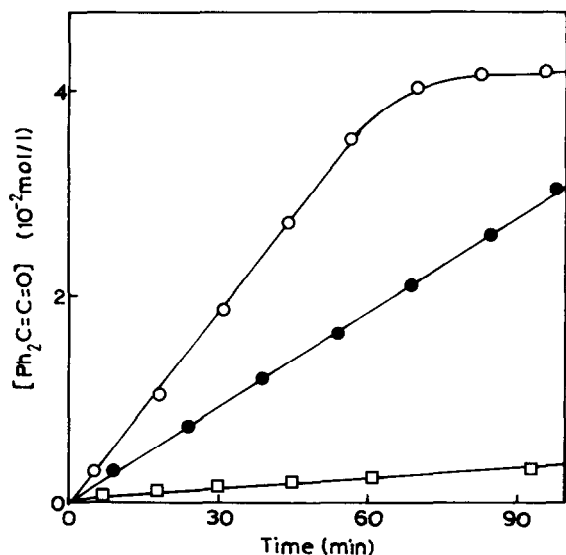


Fig. 1. Relation between reaction time and diphenylketene concentration. Reaction conditions; Ph_2CHCOCl 0.28 mol/l, platinum complexes 0.055 mol/l, in benzene 5 ml, 29°C, CO 1 atm. ○, 1; ●, 4; □, 5.

fixed in the presence of a large excess of PPh_3 , the initial rate was found to be almost independent of the initial platinum complex concentration (Fig. 3). In addition when the concentrations of Ph_2CHCOCl and platinum complex are constant, addition of PPh_3 to the reaction system clearly increased the rate (Fig. 4).

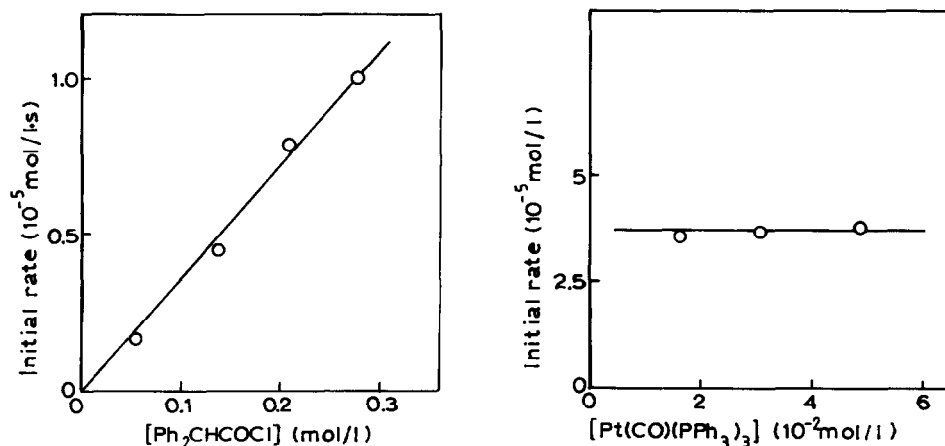


Fig. 2. Effect of concentration of Ph_2CHCOCl on the reaction. Reaction conditions; $\text{Pt}(\text{PPh}_3)_4$ 0.055 mol/l, in benzene 5 ml, 29°C, CO 1 atm.

Fig. 3. Effect of concentration of platinum complex on the reaction. Reaction conditions; Ph_2CHCOCl 0.24 mol/l, PPh_3 0.19 mol/l, in benzene 5 ml, 29°C, CO 1 atm. Because 4 is the major platinum species in a solution containing excess PPh_3 under CO [11], 4 was used as the platinum species charged, instead of 1, in order to minimize the change of PPh_3 concentration by PPh_3 dissociation.

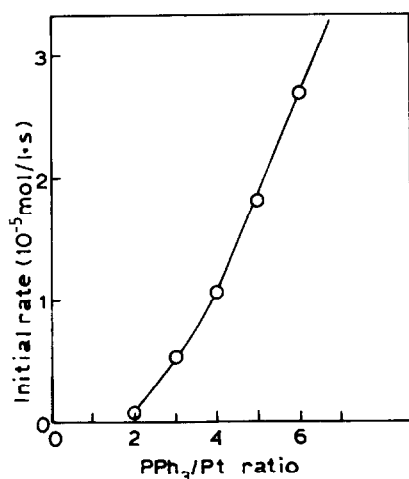


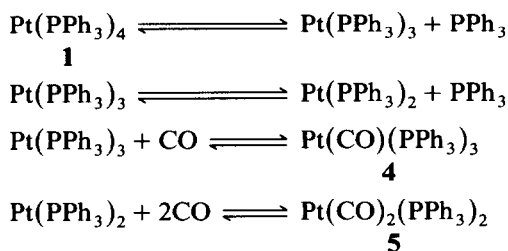
Fig. 4. Effect of PPh_3/Pt ratio on the reaction. Reaction conditions; Ph_2CHCOCl 0.28 mol/l, platinum complexes 0.055 mol/l, in benzene 5 ml, 29°C , CO 1 atm. 5, 4, and 1 were used as the platinum species charged where PPh_3/Pt were 2, 3, ≥ 4 , respectively.

Unfortunately, the precise concentration of free PPh_3 could not be determined by ^{31}P NMR because 1 showed only a broad signal under N_2 , or under CO, at r.t. owing to fast phosphine exchange. However, according to the equilibrium shown in Scheme 2, it may be assumed that 4 which contains 3 molecules of PPh_3 is the major platinum species at high PPh_3/Pt ratios under CO [11]. The initial rate is almost proportional to the value $(\text{PPh}_3/\text{Pt}) - 3$ at high PPh_3/Pt ratio. This indicates that the initial rate is first order in the free PPh_3 concentration $[\text{PPh}_3]$. The deviation from linearity at low PPh_3/Pt ratio is probably due to PPh_3 dissociation from 4 to form 5. The rate expression was estimated from the kinetic data to be:

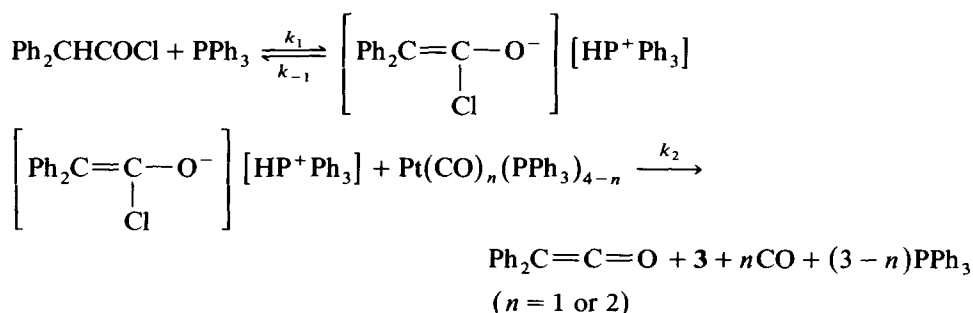
$$\text{rate}_{\text{obsd}}(d[\text{Ph}_2\text{C}=\text{C}=\text{O}]/dt) = k[\text{Ph}_2\text{CHCOCl}][\text{PPh}_3] \quad (1)$$

$$k = (7.1 \pm 1.2) \times 10^{-4} \text{ l/mol} \cdot \text{s (at } 29^\circ\text{C)}$$

Furthermore, a primary kinetic isotope effect ($k_{\text{H}}/k_{\text{D}} = 4.5$) was observed in the reaction of 2-deuteriodiphenylacetyl chloride at 29°C , which suggests that the rate-determining step is the $\alpha\text{-C-H}$ bond cleavage in Ph_2CHCOCl .



Scheme 2



Scheme 3

A possible mechanism which is consistent with the kinetic data is depicted in Scheme 3. The first step is the rate-determining enolization of Ph_2CHCOCl by PPh_3 . Participation of an enol phosphonium salt has been assumed in the diphenylketene formation from α -bromodiphenylacetyl bromide and PPh_3 [12]. Since the reaction of Ph_2CHCOCl with PPh_3 produced no changes in the IR and ^1H NMR spectra as mentioned above, k_1 must be far smaller than k_{-1} . The second step is the fast formation of diphenylketene and 3 by the reaction of a platinum carbonyl complex $\text{Pt}(\text{CO})_n(\text{PPh}_3)_{4-n}$ ($n = 1$ or 2) with the enolized Ph_2CHCOCl . Carbonyl ligands diminish the nucleophilicity of the platinum and prevent the oxidative addition of Ph_2CHCOCl to give 2. However, the platinum complex is basic enough to abstract the proton from HP^+Ph_3 . Subsequent Cl^- abstraction from the Ph_2CHCOCl enolate anion results in the formation of 3 and diphenylketene.

The rate equation obtained by applying the steady-state treatment with respect to the enolized Ph_2CHCOCl in Scheme 3 is described as follows:

$$\text{rate}_{\text{calcd}} = \frac{k_1 k_2 [\text{Ph}_2\text{CHCOCl}] [\text{PPh}_3] [\text{Pt}(\text{CO})_n(\text{PPh}_3)_{4-n}]}{k_1 [\text{Ph}_2\text{CHCOCl}] + k_{-1} + k_2 [\text{Pt}(\text{CO})_n(\text{PPh}_3)_{4-n}]} \quad (2)$$

Assuming that $k_2 [\text{Pt}(\text{CO})_n(\text{PPh}_3)_{4-n}] \gg k_1 [\text{Ph}_2\text{CHCOCl}]$, k_{-1} , eq. 2 can be approximated as follows:

$$\text{rate}_{\text{calcd}} = k_1 [\text{Ph}_2\text{CHCOCl}] [\text{PPh}_3] \quad (3)$$

This is in agreement with the observed rate expression eq. 1.

Interestingly, a cationic ruthenium acyl complex was previously considered to be an intermediate in the ketene formation by the reactions of acid chlorides and a ruthenium carbonyl complex [5]. Mechanisms including β -hydrogen elimination of the acyl ligand or proton dissociation from the acyl complex have been proposed. However, in the case of platinum, mechanisms involving platinum acyl complexes are unambiguously excluded because the reaction rate is independent of the platinum complex concentration. The fact that 2 did not liberate diphenylketene under CO in benzene also supports the argument above.

Finally, the Arrhenius plot of k_1 is shown in Fig. 5, for which the equilibrium of Scheme 2 was assumed to be unchanged over the temperature range of 10–50°C. The overall activation energy was determined to be 11.9 ± 1.4 kcal/mol.

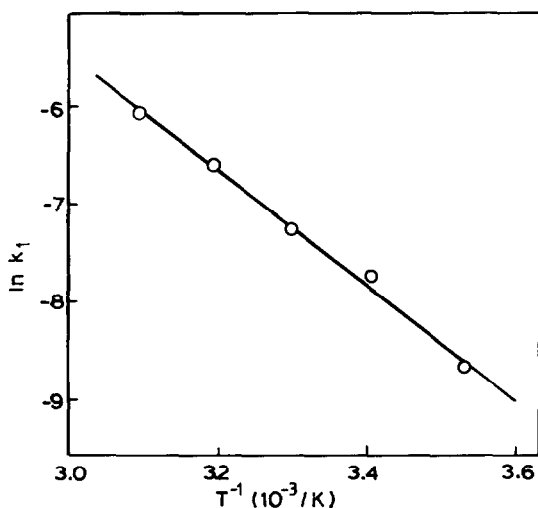


Fig. 5. Arrhenius plot of k_1 . Reaction conditions; Ph_2CHCOCl 0.28 mol/l, $\text{Pt}(\text{PPh}_3)_4$ 0.055 mol/l, in benzene 5 ml, CO 1 atm.

The results described here reveal the novel reactivity of low-valent platinum complexes and provide important information on the mechanism for ketene formation from acid chlorides and platinum complexes. Participation of the ketene formation in catalytic reactions such as the cyclocarbonylation [7,8] is now under investigation.

Experimental

The ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded on a JEOL GX-400 spectrometer at 400 MHz and 161.8 MHz, respectively. Chemical shifts are relative to internal TMS and external H_3PO_4 , respectively. Infrared spectra were taken on a JASCO IR-810 spectrophotometer.

The reactions were performed under N_2 or CO by Schlenk tube techniques. $\text{Pt}(\text{PPh}_3)_4$ [13], $\text{Pt}(\text{CO})(\text{PPh}_3)_3$ [11], $\text{Pt}(\text{CO})_2(\text{PPh}_3)_2$ [11], $\text{Pt}[\text{P}(\text{OPh})_3]_4$ [14], $\text{Pd}(\text{PPh}_3)_4$ [15], and $\text{Pd}(\text{CO})(\text{PPh}_3)_3$ [16] were prepared by published methods. Diphenylacetyl chloride, 2-deuteriodiphenylacetyl chloride, and 2-phenylpropionyl chloride were prepared by the reaction of diphenylacetic acid, 2-deuteriodiphenylacetic acid [17], and 2-phenylpropionyl chloride, respectively, with SOCl_2 [18]. All solvents used were purified by standard methods and stored under N_2 or CO .

Reaction of acid chlorides and platinum or palladium complexes

The following procedure for the reaction of Ph_2CHCOCl with **1** under CO is representative. In a measuring flask was placed a benzene solution (5 ml) of Ph_2CHCOCl (240 mg, 1.04 mmol) and **1** (343 mg, 0.276 mmol), and the flask was set in a round bottom flask settled in a thermostated oil bath under CO . A small portion of the solution was withdrawn with a syringe every 10–15 min, and diphenylketene in the solution was determined by measuring IR the absorption at

2100 cm^{-1} . The initial reaction rate was determined from the linear part of the time–diphenylketene concentration curve.

In a separate reaction of Ph_2CHCOCl (347 mg, 1.5 mmol) with **1** (623 mg, 0.50 mmol) in toluene (10 ml) under CO during 4 h at r.t., *trans*- $\text{PtHCl}(\text{PPh}_3)_2$ (**3**) [19] (336 mg, 89%) was obtained by adding hexane to the reaction mixture: ^1H NMR (CD_2Cl_2) δ -16.19 (t, 1 H, Pt–H, $^2J(\text{P–H}) = 13.75$ Hz, $^1J(\text{Pt–H}) = 1195$ Hz), 7.4–7.7 (m, 30H, Ph); $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ 28.3 (s, $^1J(\text{Pt–P}) = 3012$ Hz); IR (KBr) 2220 cm^{-1} ($\nu(\text{Pt–H})$).

A reaction of Ph_2CHCOCl (0.70 g, 3.0 mmol) and **1** (1.2 g, 1.0 mmol) in toluene (40 ml) under N_2 gave the white precipitate of *trans*- $\text{PtCl}(\text{COCHPh}_2)(\text{PPh}_3)_2$ (**2**) and the solution showed no IR absorption due to diphenylketene. After removal of the solvent, recrystallization of the residual solid from CH_2Cl_2 –hexane gave *trans*- $\text{PtCl}(\text{COCHPh}_2)(\text{PPh}_3)_2 \cdot \frac{1}{2}(\text{CH}_2\text{Cl}_2)$ (0.65 g, 65%) as white crystals; ^1H NMR (CD_2Cl_2) δ 3.15 (s, 1 H, CHPh_2), 6.49–7.74 (m, 40 H, Ph); $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ 19.0 (s, $^1J(\text{Pt–P}) = 3538$ Hz); IR (KBr) 1651 cm^{-1} ($\nu(\text{C=O})$). Anal. Found: C, 60.88; H, 4.45. $\text{C}_{101}\text{H}_{84}\text{Cl}_4\text{O}_2\text{P}_4\text{Pt}_2$ calcd.: C, 61.09; H, 4.26%.

Similarly, reaction of Ph_2CHCOCl (0.90 g, 3.9 mmol) with $\text{Pd}(\text{PPh}_3)_4$ (1.5 g, 1.3 mmol) in benzene (40 ml) afforded *trans*- $\text{PdCl}(\text{COCHPh}_2)(\text{PPh}_3)_2$ (0.92 g, 82%) as yellow crystals: ^1H NMR (CD_2Cl_2) δ 3.75 (s, 1 H, CHPh_2), 6.62–7.73 (m, 40 H, Ph); $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ 18.6 (s); IR (KBr) 1670 cm^{-1} ($\nu(\text{C=O})$).

Acknowledgment

We gratefully acknowledge financial support by the Ministry of Education of Japan.

References

- 1 A. Takeuchi and J.R. Katzer, *J. Phys. Chem.*, **86** (1982) 2438; E.L. Muetterties and J. Stein, *Chem. Rev.*, **79** (1979) 479; W.A. Herrmann, *Angew. Chem. Int. Ed. Engl.*, **21** (1982) 117; P.T. Wolczanski and J.E. Bercaw, *Acc. Chem. Res.*, **13** (1980) 121.
- 2 A. Miyashita, T. Kihara, N. Nomura, and H. Nohira, *Chem. Lett.*, (1986) 1607; A. Miyashita, K. Nomura, S. Kaji, and H. Nohira, *Chem. Lett.*, (1989) 1983; T. Mitsudo, H. Watanabe, T. Sasaki, Y. Takegami, Y. Watanabe, K. Kafuku, and K. Nakatsu, *Organometallics*, **8** (1989) 368; K.H. Dötz in A. de Meijere and H. tom Dieck (Eds.), *Organometallics in Organic Synthesis*, Springer-Verlag, Berlin, 1988, p. 85; W.D. Wulff in L.S. Liebeskind (Ed.), *Advances in Metal-Organic Chemistry*, Vol. 1, Jai Press Inc., Greenwich, 1988, p. 209.
- 3 G.L. Geoffroy and S.L. Bassner in F.G.A. Stone and R. West (Eds.), *Advances in Organometallic Chemistry*, Vol. 28, Academic Press, San Diego, 1988, p. 1; A. Miyashita, *J. Synth. Org. Chem., Jpn.*, **46** (1988) 135.
- 4 R.S. Ward in S. Patai (Ed.), *the Chemistry of Ketenes, Allenes and Related Compounds*, Part 1, Wiley, New York, 1980, p. 223.
- 5 S.I. Hommeltoft and M.C. Baird, *Organometallics*, **5** (1986) 190.
- 6 S. Singh and M.C. Baird, *J. Organomet. Chem.*, **338** (1988) 255.
- 7 H. Matsuzaka, Y. Hiroe, M. Iwasaki, Y. Ishii, Y. Koyasu, and M. Hidai, *J. Org. Chem.*, **53** (1988) 3832; M. Iwasaki, H. Matsuzaka, Y. Hiroe, Y. Ishii, and M. Hidai, *Chem. Lett.*, (1988) 1159.
- 8 M. Iwasaki, Y. Kobayashi, J. Li, H. Matsuzaka, Y. Ishii, and M. Hidai, *J. Org. Chem.*, in press.
- 9 C.D. Cook and G.S. Jauhal, *Can. J. Chem.*, **45** (1967) 301.
- 10 J.E. Baldwin and J.D. Boberts, *J. Am. Chem. Soc.*, **85** (1963) 2444.
- 11 P. Chini and G. Longoni, *J. Chem. Soc. (A)*, (1970) 1542.
- 12 S.D. Darling and R.L. Kidwell, *J. Org. Chem.*, **33** (1968) 3974.
- 13 R. Ugo, F. Caliat, and G. La Monica, *Inorg. Synth.*, **11** (1968) 105.

- 14 J.J. Levison and S.D. Robinson, *Inorg. Synth.*, 13 (1972) 109.
- 15 D.R. Coulson, *Inorg. Synth.*, 13 (1972) 121.
- 16 K. Kudo, M. Hidai, and Y. Uchida, *J. Organomet. Chem.*, 33 (1971) 393.
- 17 J.G. Atkinson, J.J. Csakvary, G.T. Herbert, and R.S. Stuart, *J. Am. Chem. Soc.*, 90 (1968) 498.
- 18 H. Staudinger, *Chem. Ber.*, 44 (1911) 1619.
- 19 J. Chatt and B.L. Shaw, *J. Chem. Soc.*, (1962) 5075; A. F. Clemmit and F. Glockling, *J. Chem. Soc. (A)*, (1969) 2163.