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Efficient Nickel Based Catalyst for the Homogeneous Reduction of Aromatic Nitro Compounds

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Abstract

The reduction of aromatic nitro compounds under CO under relatively mild conditions in the presence of NiX_2L_2 (X = Cl, Br, I; L = PR_3, R = Me, Et, Ph) and $NiI_2(PhNH_2)_4$ as catalyst precursors is described. The nitrobenzene is quantitatively converted into *N,N'* diphenylurea in aniline solution and into alkylcarbanylate with a good yield, in aniline–alcohol mixtures. Nitrobenzene derivatives (p-$RC_6H_4NO_2$; R = CH_3, Cl) and 2,4-dinitrotoluene, are also reduced in aniline solution; diphenylurea and amine, corresponding to the nitroderivatives, are the reaction products in these cases. This different behaviour is explained in terms of aminolysis of the expected *N*-aryl-*N'*-phenylurea. Sufficient data are produced to say that the observed increase of the catalytic activity, increasing in the sequence Cl, Br, I by changing the NiX_2L_2 complex, is due to an additional co-catalytic effect of the halide. On the basis of the chemical behaviour and IR evidence, the true catalytic species and some intermediates of reaction are suggested and a possible catalytic cycle is discussed.

Introduction

The synthesis of diarylureas and carbamates, via reductive carbonylation of aromatic nitro compounds, is generally accomplished under rather drastic conditions and using a system based on salts or complexes of noble metals [1, 2]. The need to find less drastic experimental conditions or less expensive catalysts has kept the subject topical. As a continuation of our studies on the reduction of nitro and nitroso compounds [3], we present in this paper** the first catalytic system based on nickel, which is very active in the homogeneous reductive carbonylation of aromatic nitro compounds.

Results and Discussion

The nitrobenzene was converted in crystalline *N,N'*-diphenylurea according to reaction (1)

$$PhNO_2 + 3CO + PhNH_2 \longrightarrow CO(NHPh)_2 + 2CO_2 \qquad (1)$$

when it was allowed to react with carbon monoxide in aniline solvent, in the presence of a catalytic amount of tertiary phosphine or aniline nickel(II) complex. The reaction proceeded rapidly when carried out at 150–180 °C under carbon monoxide pressures higher than 20 atm and yielded about 95% diphenylurea. Lower pressures were also efficient, but a non-characterized dark violet product was obtained as well as *N,N'*-diphenylurea. Nickel complexes of formula NiX_2L_2 or NiX_2COL_2 (X = Cl, Br, I; L = PR_3; R = Me, Et, Ph) were tried as catalyst precursors. $NiI_2(PhNH_2)_4$ was also very efficient. Small differences in catalytic activity were observed by changing the phosphine ligands (Table I, run 1–3). An increasing reaction rate was noted by changing the halide bonded to the nickel to Cl and I (run 3–5). Better results were obtained with $NiI_2(PPh_3)_2$ or $NiI_2(PhNH_2)_4$ at 180 °C and 40 atm (run 1, 6). An explanation for the halide influence will be given later.

The nitrobenzene derivatives p-R-$C_6H_4NO_2$ (R = Me, Cl) and the 2,4-dinitrotoluene were also deoxygenated under the same conditions. However, *N,N'*-diphenylurea and the amine corresponding to the aromatic nitro compounds (reaction (2)) were the conversion products (run 14, 15, Table I).

$$p\text{-R-}C_6H_4NO_2 + 3CO + 2PhNH_2 \xrightarrow{PhNH_2} p\text{-R-}C_6H_4NH_2 + CO(NHPh)_2 + 2CO_2 \qquad (2)$$

Ni-halides have been used, in drastic conditions, for the catalysed carbonylation of amines [5]. Control experiments showed that, under the reaction conditions, diphenylurea is not produced in the absence of the nitro compound and that no reaction was observed when aniline was allowed to interact at

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**See also ref. 4.

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TABLE I. Reductive Carbonylation of Aromatic Nitro Compounds into *N,N'*-diphenylurea (T = 180 °C, P_{CO} = 40 atm)

Run	Catalyst[a]	R in $4\text{-}RC_6H_4NO_2$[a]	Solvent	Time (h)	Nitro-conversion (%)	Diphenylurea (%) selectivity
1	$NiI_2(PPh_3)_2$ (0.12)	H (9.76)	$PhNH_2$	2	90	98
2	$NiI_2(PEt_3)_2$ (0.12)	H (9.76)	$PhNH_2$	2	80	97
3	$NiI_2(PMe_3)_2$ (0.15)	H (9.76)	$PhNH_2$	2	60	95
4	$NiBr_2CO(PMe_3)_2$ (0.13)	H (9.76)	$PhNH_2$	13	54	67
5	$NiCl_2(PMe_3)_2$ (0.12)	H (9.76)	$PhNH_2$	13	50	65
6	$NiI_2(PhNH_2)_4$ (0.12)	H (9.76)	$PhNH_2$	2	85	97
7	$Ni(CO)_2(PPh_3)_2$ (0.16)	H (9.76)	$PhNH_2$	4	20	97
8	$Ni(CO)_2(PPh_3)_2$ (0.16) + I^- (1.24)[b]	H (9.76)	$PhNH_2$	2	99	96
9	$Ni(CO)_2(PPh_3)_2$ (0.16) + Br^- (1.33)[c]	H (9.76)	$PhNH_2$	4	58	98
10	$Ni(CO)_2(PPh_3)_2$ (0.16) + Cl^- (1.31)[d]	H (9.76)	$PhNH_2$	4	53	98
11	$NiI_2(PPh_3)_2$ (0.12)	H (9.76)	C_6H_6	15	–	–
12	$NiI_2(PPh_3)_2$ (0.12)	H (9.76)	Py	13	34	[e]
13	$NiI_2(PPh_3)_2$ (0.12)	H (9.76)	NEt_3	10	48	[f]
14	$NiI_2(PPh_3)_2$ (0.12)	CH_3 (7.30)	$PhNH_2$	3	91	98[g]
15	$NiI_2(PPh_3)_2$ (0.12)	Cl (5.08)	$PhNH_2$	3	83	97[h]
16	$NiBr_4(HPPh_3)$ (0.15)	H (9.76)	$PhNH_2$	3	59	97
17	$NiI_4(HPPh_3)_2$ (0.15)	H (9.76)	$PhNH_2$	2	95	98

[a] mmol in parentheses [b] Added as $Et_3CH_3N^+I^-$. [c] Added as $(CH_3)_4N^+Br^-$. [d] Added as $(CH_3)_4N^+Cl^-$. [e] 80% of the nitro reacted was converted into aniline. [f] 70% of the nitro reacted was converted into aniline. [g] *p*-toluidine was detected in solution. [h] *p*-chloroaniline was detected in solution.

TABLE II. Reductive Carbonylation of Nitrobenzene into Alkylcarbanylates (T = 180 °C, P_{CO} = 40 atm)

Run[a]	Catalyst	Solvent	Time (h)	Nitrobenzene conversion (%)	CO(NHPh)(OR) (%) selectivity
1	$NiI_2(PPh_3)_2$ (0.12)	EtOH	13	50	10
2	$NiI_2(PPh_3)_2$ (0.12)	$EtOH/PhNH_2$ (14:1)	13	64	72
3	$NiI_2(PPh_3)_2$ (0.12)	$C_6H_6/EtOH/PhNH_2$ (14:4:1)	4	34	55
4	$NiI_2(PPh_3)_2$ (0.12)	$C_6H_6/MeOH/PhNH_2$ (14:4:1)	3	58	40
5	$NiI_2(PhNH_2)_4$ (0.15)	$C_6H_6/EtOH/PhNH_2$ (14:4:1)	13	92	44

[a] In all the experiments 9.76 mmol of nitrobenzene and 9 ml of solvent were used.

180 °C with carbon dioxide pressure (8 atm). Thus, it is reasonable to assume that the reaction (2) proceeds via conversion of the nitro compound into *N*-aryl-*N'*-phenylurea and successive aminolysis of the latter to arylamine and diphenylurea (reaction (3) and (4)).

$$p\text{-}R\text{-}C_6H_4NO_2 + 3CO + PhNH_2 \longrightarrow p\text{-}R\text{-}C_6H_4NHCO(NHPh) + 2CO_2 \quad (3)$$

$$p\text{-}R\text{-}C_6H_4NHCO(NHPh) + PhNH_2 \longrightarrow CO(NHPh)_2 + p\text{-}R\text{-}C_6H_4NH_2 \quad (4)$$

The equilibrium (4), in aniline solution, is practically shifted to the right. This view is in agreement with the fact that, by carrying out the reaction in aniline–benzene solution, *N*-aryl-*N'*-phenylurea and diphenylurea mixtures were produced. Under these conditions, however, the progress of the reaction was slow.

With the aim of converting the nibrobenzene in carbamates, we performed the reaction in alcohol solution under the same conditions of temperature and pressure. In this case, the reaction was slower, and the selectivity in alkyl carbanylate was low (Table II, run 1). Aniline and *N*-alkyl-aniline (coming probably from the reaction between aniline and alcohol) were the other reaction products. However, by adding aniline (0.5 ml per 7 ml of alcohol), the yield of carbamate increased (Table II, run 2). Good yields were also obtained by carrying out the reaction in benzene–alcohol mixtures in the presence of aniline (run 3–8, Table II). Under these conditions, side products such as alkyl-anilines were not produced. We think that the increased yield in uretane, obtained in presence of aniline, is not caused by an increasing rate of its synthesis reaction (5).

$$PhNO_2 + 3CO + ROH \longrightarrow PhNHCOOR + 2CO_2 \quad (5)$$

It is probable, instead, that the carbamate is due to the alcoholysis of the *N,N'*-diphenylurea (reaction (6)), coming via reaction (1).

$$CO(NHPh)_2 + ROH \longrightarrow NHPhCOOR + PhNH_2 \quad (6)$$

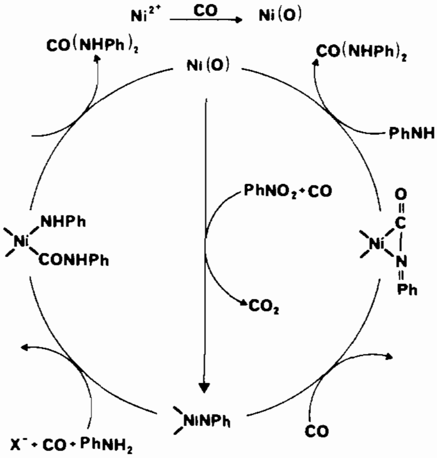
Support for this view is supplied by the presence of some amounts of urea in the reaction products. Furthermore, by increasing the aniline/alcohol ratio, the amount of urea increases. Control experiments showed that, under reaction conditions, the ethylalcohol reacts with *N,N'*-diphenylurea to give ethyl carbamate.

In order to ascertain the nature of the true catalytic species and the mechanism of the reaction, the catalysis was carried out in the presence of an Ni(0)–carbonyl complex. This was suggested by observing that when an aniline solution of $NiI_2(PPh_2)_3$ reacts with CO at 100 ℃, with or without nitrobenzene, the IR spectrum displays bands at 2065(m) and 1990(s) cm^{-1} assignable to $Ni(CO)_3PPh_3$. An identical IR spectrum was exhibited by an aniline solution of $Ni(CO)_2(PPh_3)_2$ heated under CO atmosphere. These results are in agreement with our earlier findings on the reductive carbonylation of Ni(II)–phosphine complexes [6].

Thus, using $Ni(CO)_2(PPh_3)_2$ as catalyst, a selective conversion of nitrobenzene into diphenylurea occurred; however, the catalytic activity was less effective than for systems with Ni(II)-complexes (Table I, run 7). It is difficult to rationalize this lower catalytic activity. In fact, it is reasonable that the Ni(0)-complex is responsible for the reduction of nitro compound; thus the catalytic activity of the systems that use this species should be at least similar to that of systems using a Ni(II)-complex. Now, since the two systems are substantially different for the halide, it is likely that the latter is responsible for this behaviour. Thus, we repeated the catalysis with $Ni(CO)_2(PPh_3)_2$ in the presence of alkyl-ammonium halides such as $Et_3NCH_3^+I^-$, $But_4N^+X^-$ (X = Br, Cl), The activity increased and the results were similar to those of the Ni(II)-systems. The same sequence of reactivity, Cl < Br < I, was found (Table I, runs 8–10).

The salt complexes $NiBr_4(HPPh_3)_2$ and $NiI_4(HPPh_3)_2$ were also very efficient catalysts (run 16, 17). These results suggest that the halide must be implicated in a rate determining step (see later). In Scheme 1 a possible catalytic cycle has been depicted. It is shown that the Ni(0)-complex, that we think is the true catalyst, reacts with the nitrobenzene, giving a nitrene intermediate that is the main path for the reduction of nitro-compounds [7]. We were not able to produce direct evidence of its formation. These species, which are sometimes suggested to be present in solution, are difficult to characterize and have been isolated only in a few cases [8]. The reaction between $Ni(CO)_2(PPh_3)_2$ and nitrobenzene carried out in heptane under nitrogen at 170 ℃ provided, however, an indirect proof for its formation. In fact, the resulting oleous product, whose IR spectrum was free from the carbonyl bands of the starting Ni(0)-complex, produced, under carbon monoxide pressure in aniline–alcohol mixture, with or without $NEt_3CH_3^+I^-$, some amount of carbamate.

With the aim to produce evidence for evolution of the nitrene intermediate, we performed the catalysis in solvents less reactive than aniline. When the nitrobenzene reacted in basic solvents such as pyridine or triethylamine, we had no evidence (IR and GLC analysis) of phenylisocyanate formation. Significant amounts of aniline and deep-brown non-characterized products were obtained (run 12, 13). In benzene solution, no reduction of the nitro compound took place; trace amounts of CO_2 were, however, observed (run 11), and the IR spectrum of the solution displayed an absorption band at 1690 cm^{-1}. It is reasonable to assign this band to the CO stretching of an isocyanate of carbamoyl complex (see Scheme 1) that are the commonly accepted intermediates in the catalysed synthesis of ureas. Isocyanate complexes of nickel, with an IR band in this region, have been characterized in the solid state [9] and in solution [10]. Nickel carbamoyl complexes, which in the presence of strong bases react with aniline to give diphenylurea [10], also show an IR band in the same region. We think that the carbamoyl complex is the more probable inter-

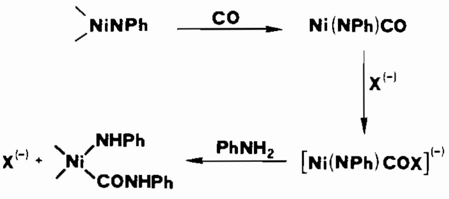


Scheme 1.

mediate; the following observations support this assumption.

(i) The most important role exercised by aniline in the catalysis could be the formation of the carbamoyl complex.

(ii) The co-catalytic role of the halide can be justified by supposing that it is directly implicated in the carbamoyl complex formation according to Scheme 2. This mechanism is similar to that recently suggested in the reductive carbonylation of nitro compounds to carbamates [11], even though a reverse sequence of reactivity in the halide was found.



Scheme 2

Conclusions

The systems described produce very efficient catalysts for the synthesis of products of practical interest. Examination of the patents and publications which have appeared in the literature [12] on this subject reveal, furthermore, that our systems should be preferred either for the relatively mild conditions or for the use of a less expensive catalyst.

Experimental

All solvents and reagents were used as purchased. Literature methods were employed for preparations of NiX_2L_2 [13], NiX_2COL_2 [14], $Ni(CO)_2(PPh_3)_2$ [15], $NiX_4(HPR_3)_2$ [16], $NiI_2(PhNH_2)_4$ [17]. $Et_3NCH_3^+I^-$ was prepared by reaction between Et_3N and CH_3I. A Carlo Erba Fractovap C gas chromatograph with a thermal conductivity detector connected to a Hewlett Packard 3380 A integrator was used. Separation of gases was achieved on Porapak Q 3.5 m column. GLC analyses were made using a Varian Vista 6000 gas chromatograph connected to a Varian 4270 integrator. A 1.5 m column SP-2250 was used for the separation of the reaction products, and biphenyl or chlorobenzene was the internal standard. Infrared spectra were recorded on a Perkin-Elmer 577 spectrophotometer with CaF_2 and KBr cells.

Catalytic Reactions with Ni(II)-complexes

(1) Reduction of nitrobenzene

(a) In aniline solution. Nitrobenzene (9.76 mmol) was charged in a 55.6 ml stainless steel autoclave together with $NiI_2(PPh_3)_2$ (0.12 mmol), aniline (8 ml) and a teflon-coated magnetic stirring bar. After that, the carbon monoxide was compressed at 40 atm; the autoclave was mounted in an electrical oven having a magnetic stirrer in its base and was heated at 180 °C for 2 h. After cooling, the gas phase was analysed (significant amounts of CO_2 were observed) and the crystalline *N,N'*-diphenylurea, present in the autoclave, was collected by filtration in air, dried under vacuum and weighed (1.82 g, 98% yield based on the reacted nitrobenzene). The filtered solution was analysed by gas chromatography and the unreacted nitrobenzene was detected (0.12 g, 10% of the starting nitrobenzene). The reactions with other catalysts were carried out according the previous procedure. The reaction times and the yields in diphenylurea were those reported in Table I.

(b) In alcohol solution. The autoclave was charged with nitrobenzene (9.76 mmol), ethanol (9 ml), $NiI_2(PPh_3)_2$ (0.12 mmol), carbon monoxide (40 atm) and was allowed to react at 180 °C for 13 h. After cooling, the gas was vented. The ethylcarbanilate (0.08 g, 10% yield based on the reacted nitrobenzene) and the unreacted nitrobenzene (4.88 mmol, 50% of starting compound) were detected by gas chromatography using chlorobenzene as internal standard. Significant amounts of *N'*-ethylaniline were also detected. The reactions in ethanol–aniline and in benzene–alcohol–aniline mixtures were performed as described above. The reaction times and the yields of the main products were those reported in Table II.

(c) In benzene solution. Nitrobenzene (9.76 mmol), $NiI_2(PPh_3)_2$ (0.12 mmol), benzene (8 ml), carbon monoxide (40 atm) were charged in an autoclave and allowed to react for 15 h at 180 °C. After cooling, the gas phase and the solution were analysed. Carbon monoxide and nitrobenzene were the only products observed.

(d) In pyridine solution. The autoclave was charged as described above using pyridine (8 ml) as solvent. After reaction (13 h), the contents of the autoclave were analysed. Significant amounts of CO_2 were observed in the gas phase; aniline (0.25 g, 80% yield based on the reacted nitrobenzene) and the unreacted nitrobenzene (0.79 g, 66% of the starting product) were detected.

(e) In triethylamine solution. The autoclave was charged as described above using 8 ml of triethylamine. After reaction (10 h), the resulting deep-brown solution contained aniline (0.30 g, 70% yield based on the reacted nitrobenzene) and unreacted nitrobenzene (0.63 g, 52% of the starting product). Trace amounts of azobenzene and a deep-brown oil product that we were not able to characterize were also obtained.

(2) Reduction of nitrobenzene derivatives

(a) In aniline solution. *p*-nitrotoluene (7.30 mmol), $NiI_2(PPh_3)_2$ (0.12 mmol), aniline (8 ml) were allowed to react for 3 h at 180 °C with carbon monoxide (40 atm). The autoclave was cooled and its content, after filtration and successive washing with benzene, gave pure *N,N'*-diphenylurea (1.5 g, 98% yield based on the reacted *p*-nitrotoluene) as confirmed by its IR spectrum. The filtered solution was analysed by gas chromatography; *p*-nitrotoluene (0.66 mmol, 9% of the starting nitro compound) and *p*-toluidine (0.50 g) were detected.

The reaction with *p*-chloro-nitrobenzene was carried out according to the above procedure. Diphenylurea and *p*-chloroaniline were the reaction products (Table I).

(b) In aniline–benzene solution. *p*-chloronitrobenzene (5.08 mmol), $NiI_2(PPh_3)_2$ (0.12 mmol), aniline (0.3 ml) and benzene (8 ml) were charged in the autoclave with carbon monoxide (40 atm) and allowed to react at 180 °C for 5 h. After cooling, the solid contents were filtered and dried under vacuum. The IR spectrum of this product was similar to that of a mixture of diphenylurea and *N*-phenyl-*N'*-chlorophenylurea. By hydrolysis of this mixture (0.20 g) in an ethanol–H_2O (1:1) solution at 170 °C, CO_2, aniline (0.11 g) and *p*-chloroaniline (0.05 g) were obtained.

(3) Reduction of 2,4-dinitrotoluene

Nitrocompound (2.71 mmol), $NiI_2(PPh_3)_2$ (0.12 mmol), aniline (8 ml) and carbon monoxide (40 atm) were allowed to react in the autoclave at 180 °C for 4 h. After cooling, the contents of the autoclave were filtered and *N,N'*-diphenylurea (0.65 g) was obtained. The filtered solution was dried under reduced pressure and after washing with heptane the residue was extracted with two 20 ml portions of acetone. By bubbling HCl, a brown product was obtained that was washed with acetone, dissolved in 20 ml of H_2O and neutralized with $NaHCO_3$. The resulting aqueous solution was filtered and extracted with two 10 ml of CH_2Cl_2. After evaporation, the extract left a solid residue; its IR spectrum was similar to that of a sample of 2,4-diaminotoluene.

Catalytic reactions

(1) with $Ni(CO)_2(PPh_3)$. The autoclave was charged with $Ni(CO)_2(PPh_3)_2$ (0.16 mmol), nitrobenzene (9.76 mmol), aniline (8 ml), carbon monoxide (40 atom) and was kept at 180 °C for 4 h. Diphenylurea (0.40 g, 97% yield based on the reacted nitrobenzene) was obtained in crystalline form, while nitrobenzene (7.81 mmol, 80% of the starting product) remained unreacted in solution.

(2) with $Ni(CO)_2(PPh_3)_2$ and $Et_3NCH_3^+I^-$. The autoclave was charged, as described in the previous reaction, in the presence of $Et_3NCH_3^+I^-$ (1.24 mmol) and was heated at 180 °C for 2 h. Diphenylurea (2.0 g, 96% yield based on the reacted nitrobenzene) was obtained while the conversion of nitrobenzene was 99%.

(3) With $Ni(CO)_2(PPh_3)_2$ and $(CH_3)_4N^+X^-$ (X = Br, Cl). The reaction was carried out according to the previous procedure. The reaction times and the yields in diphenylurea were those reported in Table I.

Test for nitrene intermediate

$Ni(CO)_2(PPh_3)_2$ (0.70 g, 1.10 mmol), nitrobenzene (0.2 ml, 1.96 mmol) and heptane (8 ml) were charged in the autoclave under atmospheric pressure of nitrogen and allowed to react at 180 °C for 5 h. After cooling, the gas phase containing large amounts of CO_2 was vented and the reaction mixture was filtered under nitrogen. The IR spectrum of the filtered solution showed a medium band at 2045 cm^{-1} and after evaporation left a small residue of triphenylphosphine oxide. The 2045 cm^{-1} band was assigned to some amounts of $Ni(CO)_4$; this was confirmed by the formation of $Ni(CO)_2(PPh_3)_2$ when triphenylphosphine was added. The brown semi-solid residue of the filtration was washed under nitrogen with heptane and dried. No bands due to unreacted $Ni(CO)_2(PPh_3)_2$ were observed in its IR spectrum. The product was introduced in the autoclave together with 9 ml of an ethanol–aniline (8:1) mixture, and carbon monoxide was compressed at 40 atm. After reaction (5 h at 180 °C), trace amounts of ethylcarbanylate were detected in solution.

Test for phenylisocyanate or carbamoyl intermediate

$NiBr_2(CO)(PMe_3)_2$ (0.35 g, 0.88 mmol), nitrobenzene (10 mmol) and C_6H_6 (10 ml) were charged in the autoclave and allowed to react with CO (40 atm) at 180 °C for 7 h. The IR spectrum of the cooled solution displayed a strong band at 1690 cm^{-1}. Aniline (0.025 g) nitrobenzene (9.1 mmol) and traces of azobenzene were detected in solution by GLC.

References

1 A. Rosenthal and I. Wender, in I. Wender and P. Pino (eds.), 'Organic Synthesis via Metal Carbonyls', Vol. 1, Interscience, New York, 1968, p. 405.

2 G. L. Rempel. W. K. Teo, B. R. James and D. V. Plackett, in D. Foster and J. F. Roth (eds.), 'Homogeneous Catalysis II, Advances in Chemistry Sereis', Vol. 132, American Chemical Society, Washington, D.C. 1974, p. 166.

3 G. Vasapollo, P. Giannoccaro, C. F. Nobile and F. Allegretta, *J. Organomet. Chem., 270,* 109 (1984); G. Vasapollo, C. F. Nobile, P. Giannoccaro and F. Allegretta, *J. Organomet. Chem., 277,* 417 (1984).

4 P. Giannoccaro and E. Pannacciulli, XVIII Congresso Nazionale di Chimica Inorganica, Como, Italy, 1985, Commun. C30.

5 Ya. Yu. Aliev, I. B. Romanova and L. Kh. Freidlin, *Uzb. Khim. Zh., 5,* 54 (1961); Ya. Yu. Aliev and I. B. Romanova, *Neftekhim Akad. Nauk. Turkm., SSR,* 204 (1963).

6 P. Giannoccaro and G. Vasapollo, *Inorg. Chim. Acta, 72,* 51 (1983).

7 A. J. Carty, *Organomet. Chem. Rev., A7,* 191 (1972).

8 H. Alpern, *Inorg. Chem., 11,* 976 (1972); E. Sappa and L. Milone, *J. Organomet. Chem., 61,* 383 (1973).

9 H. Hoberg and J. Korff, *J. Organomet. Chem., 150,* C20 (1978).

10 A. Sacco, P. Giannoccaro, G. Vasapollo, *Inorg. Chim. Acta, 83,* 127 (1984).

11 S. Cenini, M. Pizzotti, C. Crotti, F. Porta and G. La-Monica, *J. Chem. Soc., Chem. Commun.,* 1286 (1984).

12 F. L'Eplattenier, P. Matthys and F. Calderazzo, *Inorg. Chem., 9,* 342 (1970); H. A. Dieck, R. M. Laine and R. F. Heck, *J. Org. Chem., 40,* 2819 (1975); *U.S. Pat. 3 335 142* (1967) to W. B. Hardy and R. P. Bennett; Y. Takeshi, T. Shichiro and H. Kenichi, *Chem. Abstr., 78,* 43087m (1973).

13 L. M. Venanzi, *J. Chem. Soc.,* 719 (1958); O. Dahl, *Acta Chem. Scand., 23,* 2343 (1969).

14 C. S. Joly, A. Mari, A. Gleizee, M. Dartiguenave, Y. Dartiguenave and J. E. Galy, *Inorg. Chem., 19,* 2403 (1980).

15 P. Giannoccaro, A. Sacco and G. Vasapollo, *Inorg. Chim. Acta, 37,* L455 (1979).

16 I. S. Ahuja, D. H. Brown, R. H. Nuttall and D. W. Sharp, *J. Inorg. Nucl. Chem., 27,* 1105 (1964).