

Preparation of $[\text{Pt}_2(\mu\text{-Cl})_2\text{Me}_2(\text{PhC}\equiv\text{CPh})_2]$. $[\text{Pt}_2(\mu\text{-Cl})_2\text{Me}_2(\text{C}_2\text{H}_4)_2]$ (0.0801 g, 0.1464 mmol) was dissolved in CH_2Cl_2 (5 mL), and $\text{PhC}\equiv\text{CPh}$ (0.0521 g, 0.2928 mmol) in CH_2Cl_2 (5 mL) was added at 0 °C. The colorless solution immediately turned clear orange. The mixture was allowed to warm to room temperature, and evaporation of the solvent yielded an orange solid identified as $[\text{Pt}_2(\mu\text{-Cl})_2\text{Me}_2(\text{PhC}\equiv\text{CPh})_2]$ (0.1141 g, 92%); mp 81–90 °C dec. Anal. Calcd for $[\text{Pt}_2(\mu\text{-Cl})_2\text{Me}_2(\text{PhC}\equiv\text{CPh})_2]$: C, 42.51; H, 3.09. Found: C, 42.15; H, 2.95. ^1H NMR in CD_2Cl_2 , 35 °C: δ 0.90 [s, $^2J(\text{PtH}) = 86$ Hz, *MePt*], 7.44 and 8.06 [m, Ph].

Similarly were prepared complexes **6a**, yield 94%, and **6b**, yield 98%, from *trans*-stilbene and dimethyl fumarate, respectively. ^1H NMR in CD_2Cl_2 : **6a** at 35 °C, δ 0.42 [s, $^2J(\text{PtH}) = 84$ Hz, *MePt*], 5.96 [s, $^2J(\text{PtH})$ not resolved, (=CH)Pt]; **6a** at –90 °C, δ 0.30 [s, $^2J(\text{PtH}) = 84$ Hz, *MePt*], 5.69 [m, $^2J(\text{PtH})$ not resolved, Pt(*H₂C=*)], 6.15 [m, $^2J(\text{PtH})$ not resolved, Pt(*H₂C=*)]; **6b** at –90 °C, δ 0.45 [s, $^2J(\text{PtH}) = 84$ Hz, *MePt*], 4.91 [AB, $^2J(\text{PtH})$ not resolved, Pt(*HC=*)], 3.73 [s, *OMe*]. Anal. Calcd for $[\text{Pt}_2(\mu\text{-Cl})_2\text{Me}_2(\text{MeO}_2\text{CCH}=\text{CHCO}_2\text{Me})_2]$ (**6b**): C, 21.57; H, 2.85. Found: C, 21.46; H, 3.36. **6b**: mp 100–103 °C.

***trans*- $[\text{PtCl}(\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{Me})(\text{C}_5\text{H}_5\text{N})_2]$ (**9**).** Excess $\text{CF}_3\text{C}\equiv\text{CCF}_3$ was condensed into a tube containing a solution of $[\text{Pt}_2(\mu\text{-Cl})_2\text{Me}_2(\text{C}_2\text{H}_4)_2]$ (0.051 g) in CHCl_3 (5 mL), and the tube was sealed. The tube was allowed to warm to room temperature, and, after 0.5 h, the tube was opened and the insoluble polymer was removed by filtration to give a clear solution. A solution of pyridine (0.029 g) in CH_2Cl_2 (5 mL) was added, the solution was concentrated, and pentane was added to precipitate the product as a yellow solid (0.091 g). NMR in CD_2Cl_2 : ^1H , δ 1.24 [s, *MeC*]; ^{19}F , δ 40.5 [q, $^3J(\text{PtF}) = 93$ Hz, $^5J(\text{FF}) = 15$ Hz, (F_3CCPt)], 54.8 [q, $^5J(\text{FF}) = 15$ Hz, (F_3CCCPt)].

Preparation of $[\text{Pt}_2(\mu\text{-Cl})_2\text{Me}_2(\text{CO})_2]$. Carbon monoxide was bubbled through a solution of $[\text{Pt}_2(\mu\text{-Cl})_2\text{Me}_2(\text{C}_2\text{H}_4)_2]$ (0.1055 g, 0.1928 mmol) in CH_2Cl_2 (10 mL) for 5 min at 0 °C. The solution was filtered, and the solvent was removed from the filtrate to yield the product as a white solid (0.0981 g, 93%). The complex was thermally unstable both as a solid and in solution above 0 °C. NMR in CD_2Cl_2 : δ 1.24 [s, $^2J(\text{PtH}) = 76$ Hz, *MePt*]. IR in CH_2Cl_2 :

$\nu(\text{CO})$ 2040 cm^{-1} .

Preparation of *cis*- $[\text{PtMe}_2(\text{SMe}_2)(\text{CO})]$. $[\text{Pt}_2\text{Me}_4(\mu\text{-SMe}_2)_2]$ (0.1078 g, 0.1876 mmol) was dissolved in acetone (10 mL), and SMe_2 (0.0233 g, 0.3752 mmol, 27.6 μL) was added to generate *cis*- $[\text{PtMe}_2(\text{SMe}_2)_2]$. Carbon monoxide was bubbled through the solution for 5 min. Evaporation of the solvent gave the product as a beige oil which could not be solidified. IR in acetone: $\nu(\text{CO})$ 2030 cm^{-1} . ^1H NMR in acetone-*d*₆ at 35 °C: δ 0.22 [s, $^2J(\text{PtH}) = 78$ Hz, *MePt* trans to CO], 0.76 [s, $^2J(\text{PtH}) = 89$ Hz, *MePt* trans to SMe_2], 2.68 [s, $^2J(\text{PtH}) = 26$ Hz, (Me_2S)Pt].

Preparation of *fac*- $[\text{PtIME}_3(\text{SMe}_2)(\text{CO})]$ (15**).** (a) *cis*- $[\text{PtMe}_2(\text{SMe}_2)(\text{CO})]$ (0.3752 mmol) was prepared as described above in acetone-*d*₆ (5 mL), and iodomethane (23.5 μL) was added to the solution. The reaction was complete after 1 day giving *fac*- $[\text{PtIME}_3(\text{SMe}_2)(\text{CO})]$ and byproducts *fac*- $[\text{PtIME}_3(\text{SMe}_2)_2]$ and $[\text{PtIME}_3]_4$. (b) *fac*- $[\text{PtIME}_3(\text{SMe}_2)_2]$ (0.3752 mmol) was generated in acetone-*d*₆ (5 mL) by addition of iodomethane (23.5 μL) to *cis*- $[\text{PtMe}_2(\text{SMe}_2)_2]$ (0.3752 mmol). CO was bubbled through the solution for 1 min. ^1H NMR in acetone-*d*₆ at –10 °C showed that Me_2S had been displaced by CO to generate *fac*- $[\text{PtIME}_3(\text{SMe}_2)(\text{CO})]$. ^1H NMR in acetone-*d*₆ for **15** at –10 °C: δ 1.31 [s, $^2J(\text{PtH}) = 70$ Hz, *MePt* trans to I or SMe_2], 1.46 [s, $^2J(\text{PtH}) = 70$ Hz, *MePt* trans to I or SMe_2], 1.20 [s, $^2J(\text{PtH}) = 64$ Hz, *MePt* trans to CO], 2.72 [s, $^3J(\text{PtH}) = 14.5$ Hz, (Me_2S)Pt]. The same reaction can be performed in benzene, but the addition of iodomethane to *cis*- $[\text{PtMe}_2(\text{SMe}_2)_2]$ is slow in this solvent. IR in benzene for **15**: $\nu(\text{CO})$ 2090 cm^{-1} .

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Registry No. 1, 12073-36-8; 2, 90523-12-9; 3, 90523-14-1; **4a**, 90523-13-0; **4b**, 90523-20-9; **5a**, 90582-02-8; **5b**, 90582-03-9; **6a**, 90523-15-2; **6b**, 90523-16-3; 7, 90523-17-4; 8, 90523-18-5; 9, 90523-19-6; 10, 101654-06-2; 11, 79870-64-7; 12, 101654-07-3; 13, 101654-08-4; 15, 101654-09-5; $\text{CF}_3\text{C}\equiv\text{CCF}_3$, 692-50-2; *cis*- $[\text{PtMe}_2(\text{SMe}_2)_2]$, 87145-38-8; *fac*- $[\text{PtIME}_3(\text{SMe}_2)_2]$, 96413-69-3; polyethylene, 9002-88-4.

Effects of Ultrasonic Waves on the Generation and Reactivities of Some Metal Powders

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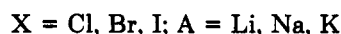
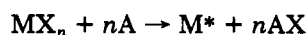
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Ultrasound substantially accelerates the lithium reductions of a variety of metal halides to metal powders. Zinc powder produced in approximately 40 min at room temperature with ultrasound demonstrates reactivity in the Reformatsky reaction which rivals zinc produced in 4 h with potassium in refluxing tetrahydrofuran. Similarly copper and nickel powders produced in approximately 40 min with ultrasound promote Ullman coupling as effectively as copper and nickel powders produced in >10 h in the presence of stirring. Results of the effect of iodide salts in the Ullman coupling of benzyl bromide are also presented.

Introduction

The field of reactive metal powders, as developed by Rieke et al., has a wide variety of synthetic applications.¹ It was found that the reduction of a metal halide with a

group 1 element (i.e., Li, Na, K) in an ethereal solvent produces a metal slurry of exceptional reactivity.



Ultrasonic waves are known to accelerate a number of heterogeneous reactions, particularly reactions involving metals.² Recently, Suslick et al.³ reported a method for

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Table I

metal powder	metal halide	reducing agent	condns ^a	red. time
Zn	ZnBr ₂	K	A	4 h ⁶
Zn	ZnBr ₂	Li	B	<40 min
Mg	MgCl ₂	K	A	1-2 h ⁷
Mg	MgCl ₂	Li	B	<40 min
Cr	CrCl ₃ ·3THF	K	A	2 h ⁸
Cr	CrCl ₃	Li	B	<40 min
Cu	CuI ₂	K	A	8 h ⁹
Cu	CuBr ₂	Li	B	<40 min

^a A = reduction in refluxing THF; B = reduction with lithium powder and ultrasound at room temperature in THF.

Table II

metal halide	red. time	
	US	stirring ¹⁰
NiCl ₂	<40 min	18 h
FeCl ₂	<40 min	24 h
PdCl ₂	<40 min	26 h
CoCl ₂	<40 min	19 h
PbCl ₂	<40 min	

the formation of metal carbonyls using metal halides, sodium sand, carbon monoxide, and high intensity ultrasonic waves. We have been conducting a related study on the accelerating effect of low intensity ultrasonic waves on the rate of reduction of metal halides to form reactive metal powders and on the reactivities of some of these powders toward organic halides.⁴ The results of these studies are present in this paper.

Results and Discussion

Generation of Powders. The reduction of metal halides with lithium can be carried out in significantly shorter periods of time with the introduction of ultrasound. Halides were reduced in one of two ways. The reductions were performed with lithium dispersion or powder and ultrasound or with lithium wire and a combination of mechanical stirring and ultrasound. Metal halides which were insoluble in THF usually required a soluble charge-transfer agent such as naphthalene⁵ (10 mol % based on

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(4) A preliminary account of these studies has been presented: Boudjouk, P.; Han, B.-H. *Abstracts of Papers*, 183rd National Meeting of the American Chemical Society, Las Vegas, NV; American Chemical Society: Washington, DC, 1982; ORGN 190.

(5) Burkhardt, E. R.; Rieke, R. D. *J. Org. Chem.* 1985, 50, 416-417. This paper reports the use of lithium naphthalide in the reduction of cadmium chloride to form a reactive cadmium powder.

Table III. Reductions in the Presence of Lithium Powders

metal halide	red. time	
	US	stirring
NiCl ₂	<40 min	14 h
NiI ₂	<40 min	12 h
CuBr ₂	<40 min	13 h
CuI	<40 min	12 h

lithium). Exposure to ultrasound was accomplished by partial submersion of the reaction flask in a Bransonic 220 bath sonicator, at a point producing maximum agitation in the flask.

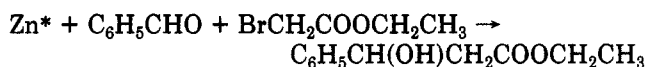
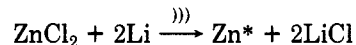
Magnesium, zinc, chromium, and copper halides can be reduced in the presence of lithium and ultrasound at a rate faster than with potassium in refluxing tetrahydrofuran (THF) as shown in Table I.

A number of other metal halides were reduced by using lithium wire and a combination of mechanical stirring and ultrasound. In all cases, reduction in the presence of ultrasound was significantly faster than in the absence of ultrasound (Table II).

We have found it more convenient to perform halide reductions in the presence of lithium powder. When mixtures of nickel or copper halides, lithium powder, and naphthalene are stirred in THF, reductions are usually complete within 12-14 h. When similar mixtures are exposed to ultrasound (in the absence of stirring), reduction is usually complete within 40 min (Table III).

Reactivities of Metal Powders. We have not investigated the reactivities of all the metal powders formed in the presence of ultrasound. However, those metal powders surveyed possess reactivities significantly greater than commercially available powders. Zinc, copper, and nickel powders produced in the presence of ultrasound possess reactivities which appear to rival powders produced by Rieke.

Zinc powder produced from ZnCl₂ and lithium dispersion in the presence of ultrasound shows exceptional reactivity in the Reformatsky reaction. For example, zinc produced in this manner will react with benzaldehyde and BrCH₂COOCH₂CH₃ by stirring in ether at room temperature. Hydrolysis after one hour results in >90% isolated yield of ethyl 3-phenyl-3-hydroxypropanoate. The same reaction run with commercially available zinc dust or granules produces a 61% yield after a 1.5 h of reflux in benzene/ether (4:1 vol/vol).^{11,12} However, the Reformatsky reaction may also be efficiently performed at room temperature with commercially available zinc powder and a catalytic amount of iodine in the presence of ultrasound.¹³



Nickel and copper powders produced in the presence of ultrasound are both capable of producing Ullman-type coupling, as demonstrated by the coupling of benzyl

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Table IV. Effect of Ultrasonic Waves on Metal Halide Reduction and Ullman Coupling

	source of Cu/Ni	reductn condns ^a	added salt ^b	stoichiometry M/RBr	Ullman condns ^c	yield, ^d %
1	CuI	US	none	3:1	5 min ref	100
2	CuI	US	none	3:1	30 min US	100
3	CuI	stir	none	3:1	30 min stir	80
4	CuI	stir	none	3:1	60 min stir	91
5	CuI	stir	none	3:1	90 min stir	95
6	CuBr ₂	US	none	3:1	30 min US	55
7	CuBr ₂	US	LiI (10%)	3:1	30 min US	77
8	CuBr ₂	US	LiI (20%)	3:1	30 min US	80
9	CuBr ₂	US	LiI (30%)	3:1	30 min US	78
10	CuBr ₂	US	none	3:1	3.5 min ref	25
11	CuBr ₂	US	LiI (20%)	3:1	3.5 min ref	55
12	CuI	US	none	3:1	3.5 min ref	85
13	CuBr ₂	US	LiI (20%)	3:1	60 min US	95
14	CuBr ₂	stir	LiI (20%)	3:1	30 min stir	38
15	CuBr ₂	stir	LiI (20%)	3:1	60 min stir	53
16	CuBr ₂	stir	LiI (20%)	3:1	12 h stir	89
17	CuBr ₂	US	LiI (20%)	3:1	30 min stir	50
18	CuBr ₂	US	LiI (20%)	3:1	60 min stir	65
19	CuBr ₂	stir	LiI (20%)	3:1	30 min US	50
20	CuBr ₂	stir	LiI (20%)	3:1	60 min US	70
21	NiI ₂	US	none	2:1	5 min ref	95
22	NiI ₂	stir	none	2:1	5 min ref	95
23	NiI ₂	US	none	2:1	30 min US	100
24	NiCl ₂	US	none	2:1	30 min US	100
25	NiCl ₂	US	none	2:1	10 min US	38
26	NiCl ₂	US	LiI (20%)	2:1	10 min US	55
27	NiI ₂	US	none	2:1	10 min US	80
28	Cu	comm ^e	LiI (20%)	3:1	8.5 h ref	0
29	Ni	comm	LiI (20%)	2:1	8.5 h ref	0

^a "US" refers to the reduction of the metal halide at room temperature in the presence of ultrasound (approximately 40 min). "Stir" refers to the reduction of the metal halide with stirring (approximately 12–14 h). ^b The presence or absence of iodide salts. In entry 7, the reduction and subsequent coupling reactions were done in the presence of lithium iodide (10 mol % with respect to the amount of lithium required to complete the reduction of the metal halide). ^c "5 min ref" refers to the performance of the Ullman coupling reaction in refluxing tetrahydrofuran. In entry 1, reduction was performed in the presence of ultrasound. After reduction was complete, the ultrasonic bath was replaced by a heating mantle and benzyl bromide was added. The mixture was then brought to reflux, and analyzed after 5 min. Similarly, "X min US" refers to the performance of Ullman coupling at room temperature with ultrasound, and "X min stir" refers to the performance of Ullman coupling at room temperature with stirring. ^d Yields via NMR. ^e Commercially available copper powder.

bromide to bibenzyl (Table IV). We have found that the nickel- or copper-induced coupling of benzyl bromide is enhanced by the presence of iodide salts. Best results occur when NiI₂ or CuI is reduced. Subsequent addition of benzyl bromide results in quantitative formation of bibenzyl within 5 min of reflux in THF¹⁴ or < 30 min of sonication. When NiCl₂ or CuBr₂ is reduced in the presence of lithium iodide, subsequent addition of benzyl bromide results in yields of bibenzyl which are substantially higher than in the absence of lithium iodide. Mixtures of commercially available nickel or copper powders, lithium iodide, and benzyl bromide in THF produce no bibenzyl after 8.5 h of reflux.

We have also compared the effects of ultrasound vs. room-temperature stirring in the Ullman coupling of benzyl bromide with copper. In Table IV, entry 2, copper iodide reduction was performed in the presence of ultrasound and then benzyl bromide added without interruption of ultrasound. Under these conditions, Ullman coupling was complete within 30 min. In entries 2 through 5, copper iodide reduction was performed with stirring and then benzyl bromide added without interruption of stirring. Under these conditions, Ullman coupling was about 80% complete after the first 30 min and about 95% complete after 90 min.

Similar results were obtained using copper bromide with added iodide salt (Table IV, entries 7, and 13 through 16). Initial Ullman coupling rates were significantly faster in the presence of continuous ultrasound, and the coupling

reactions tended to go to completion. Under continuous stirring, initial coupling rates were slower, and the coupling reactions tended to resist completion. In entries 17 and 18 (Table IV) the reduction of copper bromide was performed in the presence of ultrasound. The ultrasonic bath was then removed, benzyl bromide added, and the coupling reaction performed in the presence of stirring. Under these conditions, the coupling was apparently more efficient than in the continuous stirring case but less efficient than in the continuous ultrasound case. Similar results were obtained when copper bromide reduction was performed in the presence of stirring and subsequent benzyl bromide coupling was performed in the presence of ultrasound (Table IV, entries 19 and 20).

The effect of ultrasound in this heterogeneous reduction probably stems from acoustic cavitation.¹⁵ Ultrasound creates cavities within the solvent which expand and eventually collapse. When cavities collapse, temperature and pressure pulses are produced which will clean and pit the surfaces of the solids dispersed in the solvent. This constant exposure of clean surface area increases the reactivities of these solids (especially in the case of active metals such as lithium) enhancing the reduction.

In all cases, metal halide reduction is greatly accelerated by using ultrasound. The metal powders surveyed resulting from these accelerated reductions are substantially more reactive than commercially available powders. On comparison with published results by Rieke et al.^{9,11} it is apparent that the reactivities of zinc and copper powders

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produced in the presence of ultrasound rival the reactivities of powders produced in the absence of ultrasound. Though there are no published results on the reactivity of Rieke nickel in the Ullman coupling of benzyl bromide to bibenzyl, results obtained in our laboratory (Table IV, entries 21 and 22) indicate no reactivity difference between nickel generated in the presence or absence of ultrasound. As with other reactions involving metal powders¹⁶ the facility of the Ullman coupling of benzyl bromide to bibenzyl is not solely dependent on the powder itself but also on the presence of iodide salts. In the case of the copper-induced Ullman coupling of benzyl bromide, ultrasound significantly facilitates coupling over room-temperature stirring. This may be attributed to the ability of ultrasound to clean the surface of the copper powder.

The use of a common ultrasonic cleaner to facilitate reduction of metal halides represents an attractive modification. Reductions may be performed with substantial time savings and no increase in complexity of apparatus. We are attempting to expand the scope and synthetic applications of metal powders produced in the presence of ultrasound. We are also investigating possible means of enhancing powder reactivity.

Experimental Section

Workup of reactions were performed in air. Untreated nickel powder, when isolated, would smoke with evolution of heat on exposure to air. Unreacted metal powders were either stored under N₂ or immediately quenched with ice. Tetrahydrofuran was distilled under N₂ from sodium/benzophenone ketyl immediately before use. Benzyl bromide was distilled and protected from light. All other liquid reagents were distilled. Anhydrous MgCl₂ was prepared from magnesium turnings and 1,2-dichloroethane immediately before use. All other anhydrous metal halides were dried in a vacuum oven overnight (1 mm/80 °C) before use. Naphthalene was sublimed before use.

Proton NMR spectra were obtained by using an EM-390 spectrometer. Gas chromatographic analyses were performed on a Varian Series 2400 and a Varian Aerograph Model 920. Melting points were obtained on a Thomas capillary melting point apparatus.

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Preparation of Ethyl 3-Phenyl-3-hydroxypropanoate from Benzaldehyde, Ethyl Bromoacetate, and Zinc. In a clean, dry, single-neck, round-bottom flask equipped with N₂ inlet and condenser were placed ZnCl₂ (1.65 g, 12 mmol), THF (10 mL), and lithium dispersion (0.17 g, 24 mmol, 30% in mineral oil). The mixture was sonicated. The reduction was very vigorous, so sonication was stopped intermittently to maintain control. After 1 h, sonication was stopped, and a fine, gray, dispersion of zinc was obtained. The THF was removed in vacuo and replaced by diethyl ether (10 mL) and then the flask cooled to 0 °C. Ethyl bromoacetate (1.67 g, 10 mmol) and benzaldehyde (0.85 g, 8 mmol) were weighed separately. One-tenth of the bromo ester was added to the zinc/ether dispersion. The remaining bromo ester and benzaldehyde were mixed and added dropwise to the dispersion. After addition was complete, the mixture was warmed to room temperature and stirred vigorously for 1 h, then poured into cold water, and stirred for 15 min. Extraction with ether, drying with MgSO₄, and vacuum evaporation left a pale yellow liquid. Analysis by GLC and NMR (by comparison to an authentic sample) showed the liquid to be the desired product, 1.39 g, 90% yield based on benzaldehyde.

Synthesis of Bibenzyl from Benzyl Bromide and Copper.

In a clean, dry, three-neck round-bottom flask equipped with condenser, N₂ inlet, and rubber septum were placed CuBr₂ (3.80 g, 0.017 mol, 10% excess), lithium powder (0.22 g, 0.031 mol), THF (20 mL), and naphthalene (0.40 g, 3.1 mmol). The mixture was sonicated with swirling approximately every 15 s. Upon sonication, the mixture became blue-black and then began to boil for about 3 min. After completion of the boil, the mixture turned black with some lithium remaining at the surface. Swirling had to be continued (once every 15 s) to keep the lithium powder from moving up the sides of the flask. After 25 min, no visible lithium remained in the flask. Sonication was continued for an extra 30 min, and then benzyl bromide (0.57 mL, 0.0048 mol) was added through the septum via syringe to the brownish black solution without interruption of sonication. Sonication was continued for 30 min and then stopped. The reaction mixture was filtered and the filtrate evaporated at low pressure to remove THF. Carbon tetrachloride was added to the residue. After a second filtration to remove lithium salts, NMR analysis of the CCl₄ solution showed 50% unreacted benzyl bromide and 50% bibenzyl. A similar reaction run with copper iodide showed only bibenzyl after 30 min, which was confirmed by GLC analysis.

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Communications

Organonickel Cyanide Chemistry. Reactions of [(PhC≡CPh)Ni(CN)₂]²⁻. An Improved Synthesis of [Ni(CN)₂(CO)₂]²⁻

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Summary: The reactions of (K·18-crown-6)₂[(η²-PhC≡CPh)Ni(CN)₂] (1) with CO, P(OMe)₃, alkynes, and α-bromo-p-xylene are described. Reaction of 1 with CO provides a route to a pure, stable salt of the Ni(CN)₂(CO)₂²⁻ anion. Compound 1 is a catalyst for the trimerization of terminal alkynes.

We recently reported that crown ethers facilitate the study of the reactivity of the long known but heretofore intractable compound K₄Ni(CN)₄.¹ One compound synthesized from K₄Ni(CN)₄ using this crown ether solid-liquid-phase transfer strategy was (K·18-crown-6)₂[(η²-PhC≡CPh)Ni(CN)₂] (1), a rare example of a stable organonickel cyanide complex and the first member of the well-known (alkyne) NiL₂ class of compounds with L = CN⁻. Because of the novelty of 1, its chemical reactivity is of interest. We have examined the reactivity of 1 and report the initial results of a study of the ligand substitution chemistry of 1. Of special interest are the discoveries that 1 is a precursor to a new, particularly tractable

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