

## Cleavage of Carbon–Metal Bonds, A Possible Explanation for the Disfavoured Coupling of Carbon and Heteroatoms by Reductive Elimination

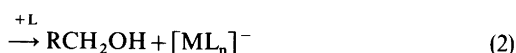
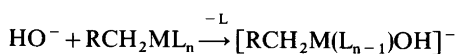
B. ÅKERMARK,<sup>a</sup> M. ALMEMARK<sup>b</sup> and A. JUTAND<sup>a,\*</sup>

<sup>a</sup> Department of Organic Chemistry, Royal Institute of Technology, S-100 44 Stockholm, Sweden and

<sup>b</sup> Swedish Water and Air Pollution Research Institute (IVL), P.O. Box 21060, S-100 31 Stockholm, Sweden

The dimethyl cobalt complexes CpCo(CH<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>) (1) (CH<sub>3</sub>)<sub>2</sub>Co(DO)(DOH)pn (2) and (CH<sub>3</sub>)<sub>2</sub>Co(2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene) (3) have been oxidized electrolytically in the presence of nucleophiles. No reaction takes place between the methyl groups and the nucleophiles. With 1, reductive elimination is the major reaction. Attempts to effect carbon–oxygen coupling by reductive elimination from phenylheterocuprates (4) failed, except when excess acetate was added as heteroatom ligand. In the reactions of heterocuprates, reductive elimination with carbon–carbon bond formation is the major reaction. It is suggested that the difference in oxidation potentials of carbon and hetero atom ligands is responsible for the result.

The formations of carbon–oxygen and carbon–nitrogen bonds are common and useful reactions, that are usually accomplished by nucleophilic substitution at carbon. Common leaving groups are stable anions such as halide or tosylate. In principle, metal ions could also act as leaving groups. For instance, a metal alkyl could be transformed into alcohol, the reaction (1), if the attack of hydroxide on carbon were sufficiently rapid to compete with other types of cleavage of the metal–carbon bond and attack on the metal. Even when attack on the metal is preferred, carbon–oxygen bond formation is, in principle, possible by reductive elimination, path (2).



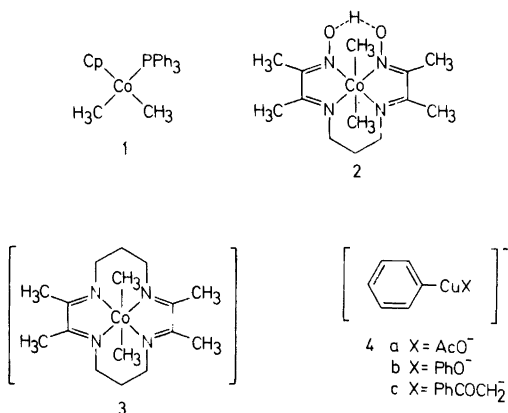
Since metal alkyls may be intermediates in catalytic activation of hydrocarbons by metals,<sup>2</sup> reactions of the types (1) and (2) offer potential routes to selective oxidation of hydrocarbons. The formation of alkylmetal hydrides, the first step in the anticipated activation process, is probably thermodynamically unfavourable (*cf.* Ref. 3 h). An oxidation process based on the reactions (1) and (2) thus requires that they be very efficient.

Although there are a few examples in the literature of reactions of the type (1), these involve only monoalkylmetals.<sup>3</sup> Furthermore, there are no clear-cut examples of reaction (2) although reactions like the Ullmann biarylether synthesis have been postulated to be of this type.<sup>4</sup> In an exploratory study we have therefore tried to evaluate the feasibility of the reactions (1) and (2) by studying a few stable model system 1–4, which were made to react by means of oxidation.

### RESULTS AND DISCUSSION

In order to evaluate the redox potentials of compounds 1–4 and also get an idea of their chemical properties after oxidation, the compounds were first studied by cyclic voltammetry. They are all irrevers-

\* See Ref. 1.



ibly oxidized at room temperature due to rapid decomposition of the oxidized intermediate. At temperatures below 0°C the oxidation of the compound 1 becomes reversible. The oxidation potentials for the compounds 1–3 (Table 1) vary between +0.29 and +0.61 V vs. Ag|AgCl|LiCl(aq) (+0.57–+0.89 V vs. standard hydrogen electrode). On oxidative decomposition, 1–3 give product cobalt complexes, which are oxidized at a higher potential. For 1, the decomposition product is reversibly oxidized even at room temperature, while the product from 2 is reversibly oxidized at –25°C. Compound 4a, showed only a poorly structured oxidation peak at around +0.5 V vs. Ag|AgCl.

Table 1. Cyclic voltammetry of compounds 1–4a.

Compound	Temp. °C	$E_p^a$ Anodic	$E_p^a$ Cathodic	$E_p$ , decomposition product Anodic	$E_p$ , decomposition product Cathodic
1	20	0.34 <sup>b</sup>	—	0.50	0.40
	–8	0.38 <sup>b</sup>	0.28	—	—
	–40	0.41 <sup>b</sup>	0.24	—	—
	20	0.29 <sup>c</sup>	—	—	—
2	20	0.55 <sup>b</sup>	—	1.5	—
	–65	0.61 <sup>b</sup>	—	1.54	1.47
	20	0.43 <sup>c</sup>	—	1.6	—
	–25	0.48 <sup>c</sup>	—	1.56	1.50
3	20	0.40 <sup>c</sup>	—	0.80	—
4a	20	~0.5 <sup>d</sup>	—	—	—

<sup>a</sup>V relative to Ag|AgCl 0.1 M LiCl (aq). <sup>b</sup>In CH<sub>2</sub>Cl<sub>2</sub>. <sup>c</sup>In acetonitrile. <sup>d</sup>In THF.

Table 2. Anodic oxidation of the complexes 1–3.<sup>a</sup>

Compound	Solvent	Potential <sup>b</sup> V	Charge passed <sup>c</sup> F/mol	Yield of gaseous products as found above the solution <sup>d</sup>		Estimated total yield of <sup>e</sup>	
				CH <sub>4</sub> , %	C <sub>2</sub> H <sub>6</sub> , %	CH <sub>4</sub> , %	C <sub>2</sub> H <sub>6</sub> , %
(1)	CH <sub>2</sub> Cl <sub>2</sub> + H <sub>2</sub> O	0.6–1	0.9 ± 0.1	0	≈ 10	0	25
	CH <sub>2</sub> Cl <sub>2</sub> + Bu <sub>4</sub> NBr	0.3–0.4	0.9 ± 0.1	0	9	0	36
	CH <sub>3</sub> CN + Bu <sub>4</sub> NOH(aq)	0.1–0.4	4 ± 0.5	0	13	0	26
(2)	CH <sub>3</sub> CN + H <sub>2</sub> O	0.45–1	1 ± 0.1	5	3	6	6
	CH <sub>3</sub> CN + H <sub>2</sub> O	0.4–0.8	0.5 <sup>f</sup>	4	1	5	2
(3)	CH <sub>3</sub> CN	0.8–0.9	≈ 1 <sup>g</sup>	4	1	5	2
	CH <sub>3</sub> CN	0.3–0.7	0.6 <sup>f</sup>	4	traces	≈ 5	traces
	CH <sub>3</sub> CN + Bu <sub>4</sub> NBr	0.7–1	1.2 ± 0.1 <sup>g</sup>	4	traces	≈ 5	traces
	CH <sub>3</sub> CN + Bu <sub>4</sub> NBr	0.3–0.5	≈ 2	1.6	0	≈ 2	0

<sup>a</sup>On a Pt foil anode, supporting electrolyte 0.1 M Bu<sub>4</sub>NBF<sub>4</sub>. <sup>b</sup>With ref. to Ag, AgCl|0.1 M LiCl(aq). As the electrolysis proceeded, the potential rose from the lower to the upper limit. <sup>c</sup>The electrolysis was continued until the anodic peak had disappeared. <sup>d</sup>Determined by GLC analysis of the atmosphere in the anodic chamber. <sup>e</sup>Corrected for solubility of methane and ethane in the solvents. <sup>f</sup>For the first anodic peak. <sup>g</sup>Total for the first and second anodic peak.

The reaction is irreversible even at low temperatures.

On oxidation at room temperature, compound *1* decomposes to give ethane as the only detectable volatile organic product (Table 2). The reaction is probably a concerted reductive elimination since methane was not detected. In the presence of nucleophiles no products other than ethane were detected except when tetrabutylammonium hydroxide was added. In this reaction small amounts of cyclopentadiene and methylcyclopentadiene were detected, but none of the desired alcohol, methanol. The latter reaction is obscure in that 4 equivalents of charge are consumed as compared to 1 equivalent in most of the other oxidations. Compounds *2* and *3* give only low yields of a mixture of methane and ethane, indicating perhaps that with these compounds, decomposition goes *via* methyl radicals. Triphenylmethylphosphonium salts may have been formed from *1* in agreement with the reaction of arylnickel halide species<sup>5a</sup> but in the presence of ionic medium it was difficult to identify. These results indicate that external nucleophilic attack on dialkylmetals is not a favourable reaction, probably both because the high electron density around the metal makes nucleophilic attack unfavourable and because reductive elimination is very efficient upon oxidation (*cf.* Ref. 5).

The preparative oxidation experiments with heterocuprates were done in THF at a potential of about +0.6 V *vs.* Ag|AgCl. The results are summarized in Table 3. The cuprates *4* were prepared *in situ* by addition of the desired nucleophile to copper(I) at -70 °C, followed by oxidation at the same temperature. Only with acetate *4a* could coupling products be detected. The major product was biphenyl, which is formed by oxidation of either polynuclear complexes or diphenylcopper(I).

The latter compound would be formed by scrambling of the phenyl and acetate groups, most probably a very rapid reaction. Interestingly, the addition of stabilized carbon nucleophiles like the enolate of acetophenone or the anion of dimethyl malonate failed to give cross coupled products with the phenyl group. The yield of the cross coupled product, phenyl acetate, is low also with the mixed phenyl-acetate complex but is increased as excess acetate is added. Even with a 5-fold excess, the yield is moderate, 20 %, and the main product is always biphenyl. Both diphenylcopper(I) and the cobalt complex *1* are thus relatively stable compounds, that after oxidation readily undergo reductive elimination. It is possible that symmetry imposed barriers to reductive elimination are important. For the mononuclear copper(I) and copper(II) species, reductive elimination is in principle forbidden, but may become allowed by cluster formation.<sup>6</sup> Especially for the copper(II) species, one could imagine the formation of a mixed copper(III)-copper(I) cluster from which reductive elimination would be permitted when the aryl groups are attached to copper(III). The stability of the cobalt complex *1* is even more surprising since the methyl groups are forced to occupy *cis*-positions. However, the most probable structures for the complex *1* are a pseudotetrahedral one with the cyclopentadienyl ring occupying only one position, or an octahedral one. For a *d*<sup>6</sup>-system like *1*, reductive elimination is symmetry forbidden for the former structure (Table 4) and permitted for the octahedral structure only when the product has a square planar configuration.<sup>6</sup> This is not possible with the cyclopentadienyl ring occupying three positions. On 1-electron oxidation, a *d*<sup>5</sup>-system is formed. Reductive elimination is still symmetry forbidden for the octahedral structure,

Table 3. Oxidation of heterocuprates *4*.

Compound	Oxidant	Potential <sup>c</sup>	Nucleophile (ratio) <sup>d</sup>	Biphenyl (yield) <sup>b</sup>	PhX (yield) <sup>h</sup>
4a	<i>a</i>	+0.6 V	NaOAc (1)	80	trace <sup>e</sup>
4a	<i>a</i>	+0.6 V	Bu <sub>4</sub> NOAc (5)	46	16 <sup>e</sup>
4b	<i>b</i>		NaOPh (5)	49	0 <sup>f</sup>
4a	<i>b</i>		Bu <sub>4</sub> NOAc (1)	80	5 <sup>e</sup>
4a	<i>b</i>		Bu <sub>4</sub> NOAc (5)	61	24 <sup>e</sup>
4a	<i>b</i>		NaOAc (2)	61	22 <sup>e</sup>
4c	<i>b</i>		LiCH <sub>2</sub> COPh (1)	62	0 <sup>g</sup>

<sup>a</sup> Electrolysis at -70 °C, THF solution, Pt-anode, supporting electrolyte LiClO<sub>4</sub>. <sup>b</sup> Air stream 2 h at -70 °C. <sup>c</sup> Relative to Ag/AgCl. <sup>d</sup> Ratio nucleophile-copper. <sup>e</sup> X=OAc. <sup>f</sup> X=OPh, none detected by GLC. <sup>g</sup> X=CH<sub>2</sub>COPh, none detected. <sup>h</sup> Based on added phenyllithium.

Table 4. Symmetry for reductive elimination from a pseudo-tetrahedral structure.

	Metal <i>d</i> -configuration	Number of electrons in orbitals of symmetry <sup>b</sup>			
		<i>a</i> <sub>1</sub>	<i>a</i> <sub>2</sub>	<i>b</i> <sub>1</sub>	<i>b</i> <sub>2</sub>
Reactant <sup>a</sup> , <i>d</i> <sup>5</sup>	$(d_{yz})^1(d_{xz-yz})^2(d_{xy})^2$	4	2	2	1
Products <i>d</i> <sup>7</sup>	$(d_{yz})^1(d_{xz})^2(d_{xz-yz})^2(d_{xy})^2$	4	2	2	1
Reactant <sup>a</sup> , <i>d</i> <sup>6</sup>	$(d_{xz})^1(d_{yz})^1(d_{xz-yz})^2(d_{xy})^2$	4	2	3	1
Products <i>d</i> <sup>8</sup>	$(d_{xz})^2(d_{yz})^2(d_{xz-yz})^2(d_{xy})^2$	4	2	2	2

<sup>a</sup> Includes the two metal-carbon orbitals. <sup>b</sup> The orbital symmetries are (*C*<sub>2v</sub>) *d*<sub>z2</sub>, *d*<sub>x2-y2</sub>: *a*<sub>1</sub>; *d*<sub>xy</sub>: *a*<sub>2</sub>; *d*<sub>xz</sub>: *b*<sub>1</sub> and *d*<sub>yz</sub>: *b*<sub>2</sub>.

but for the pseudotetrahedral it now becomes allowed (Table 4), in accordance with the experimental result.

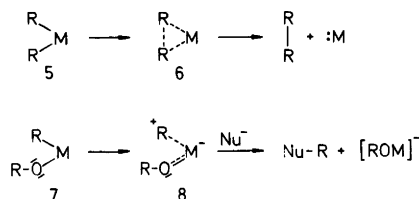
In order to investigate the carbon–oxygen coupling reaction in some further detail, we have also done a series of experiments where the arylcopper(I)–nucleophile system was oxidized by air. The results are very similar to those obtained with electrochemical oxidation. Of the nucleophiles used, phenolate, malonate, the enolate of acetophenone and acetate, only acetate couples with the phenyl group, giving phenyl acetate. The yield is low, 5%, when equimolar amounts of phenylcopper and acetate were mixed and about 20% when a 5-fold excess of acetate was added. The major product, as in the electrolyses, is biphenyl. The explanation for this result is not clear. Since diphenylcopper(I) would be expected to be oxidized at a lower potential than a mixed arylcopper acetate, continuous phenylacetate scrambling and selective oxidation of diphenylcopper would explain the result. An alternative explanation is that phenyl acetate is not formed by reductive elimination but by direct attack on the phenyl ring. Excess nucleophile is then required. The reaction could be regarded either as an attack on a phenyl cation or on a metal bound phenyl cation radical. The observed need for excess acetate ion has also been noted for the electrolytic acetoxylation of arylpalladium species generated *in situ* from arylmercury compounds.<sup>7</sup> The attack on phenyl cation is similar to reactions of alkylmetals according to path (1). In this type of reaction, the carbon attached to metal will probably have considerable carbonium ion character as indicated by phenonium ion formation from (2-phenyl)ethylpalladium species.<sup>8</sup>

Since diphenyl ether was not formed from phenylcopper and sodium phenolate, it seems unlikely that a phenylcopper phenolate is an intermediate in the

Ullmann biaryl ether synthesis. Other mechanisms which must be considered are direct nucleophilic displacement on a coordinated aryl halide and copper catalyzed oxidation of the aryl halide to a cation radical, which undergoes displacement. Both reactions have analogies, the former in the addition of nucleophiles to arenes promoted by chromium carbonyl and similar reagents<sup>9a</sup> and the latter in nucleophilic aromatic substitution catalyzed by electrolysis or strong 1-electron oxidants.<sup>9b</sup> Another possibility is, of course, the classical 4-centre mechanisms.<sup>10</sup> Further studies are clearly desirable.

Although the exact mechanism of the phenylacetate coupling is not clear, it is evident that reductive elimination is not facile. This is even more true for the other tested nucleophiles, neither of which gave detectable amounts of coupling products. This reluctance to reductive elimination has been observed earlier, for instance in the cleavage of palladium–carbon bonds by acetate, amines and chloride.<sup>3c,3d</sup> In these reactions the nucleophile is probably coordinated to the metal but the stereochemistry of the reaction shows that the external attack by free nucleophile is favoured. In contrast, alkanide ions, after coordination, preferentially undergo *intra*-molecular reaction. As noted earlier, this preference for intramolecular reaction applies also to the addition of non-stabilized carbanions to  $\pi$ -olefin and  $\pi$ -allyl systems.<sup>11</sup> Again, heteroatom nucleophiles and stabilized carbanions like malonates, prefer external attack.<sup>11</sup>

The reasons for this are not clear, but perhaps the oxidation potentials of the coordinated ligands are important. For instance, reductive elimination from a dialkyl- or diarylmethyl, could be pictured as a symmetric electron transfer from the two coordinated carbanions until one electron has been removed from each and coupling takes place. In the process, the carbanions have in principle become



Scheme 1.

oxidized to radicals. When coupling is symmetry allowed, the formation and combination of the radicals is probably concerted (eg. 5→6).

For an alkylmetal alkoxide the situation is different and we would like to suggest that the difference in the oxidation potentials for the two ligands is the most important factor. For instance, 2-methylpropanide ion is oxidized at a very much lower potential (−2.2 V) than the corresponding alkoxide, *t*-butoxide (+1.0 V).<sup>12a,b</sup> Other examples are phenylmethanide ion (−1.58 V)<sup>12a,b</sup> and acetate (+2.4 V).<sup>12a</sup> In fact, one might suspect that even carbon radicals are more readily oxidized than alkoxides since copper(II) (standard potential +0.15 V)<sup>13</sup> will oxidize carbon radicals to carbonium ions.<sup>14</sup> Furthermore, the determined oxidation potential for one member of this group, the triphenylmethyl radical, is considerably lower (+0.48 V)<sup>12a,b</sup> than that of *t*-butoxide. As electron density is transferred from the ligands to the metal, it seems reasonable that electron density is removed from the carbanion while the alkoxy group will be expected to respond by forming a partial double bond to the metal. When electron transfer has proceeded to a point where two electrons have been removed from the ligands, (7→8), the metal bound carbon has acquired carbonium ion character while the alkoxide has mainly become more strongly bound to the metal. As a result, attack by external nucleophiles, if available, will be preferred over internal migration of the coordinated alkoxide to carbon. This is in accordance with earlier experimental evidence,<sup>3</sup> including the carbonium ion character at coordinated carbon.<sup>8</sup> It is also in accordance with our observation that the coupling of phenyl and acetate *via* phenylcopper(I) is promoted by excess acetate.

In conclusion, reductive elimination involving carbon–oxygen bond formation (reaction 2) and nucleophilic substitution at the alkyl groups of dialkyl-metals (reaction 1) appear to be slow relative

to other types of reactions, e.g. reductive elimination involving carbon–carbon coupling. Other types of reactions must therefore probably be relied upon for selective oxidation of hydrocarbons.

## EXPERIMENTAL

**Materials.** The dimethylcobalt complexes 1–3 were prepared by literature procedures.<sup>15–17</sup> Tetrabutylammonium fluoroborate was prepared by mixing solutions of sodium fluoroborate (Riedel – de Haen AG, Seelze-Hannover) and tetrabutylammonium hydrogen sulfate (Bofors Nobel Kemi). The product was dissolved in dichloromethane and the solutions washed with water and dried. After evaporation of the solvent, the product was recrystallized twice from ethyl acetate – pentane and dried *in vacuo* at 80 °C over P<sub>2</sub>O<sub>5</sub> for 16 h. Tetrabutyl ammonium bromide (Eastman Kodak Co.) was recrystallized twice from ethyl acetate, then dried over P<sub>2</sub>O<sub>5</sub> overnight, first at 80 °C, then at 120 °C. Tetrabutylammonium acetate was prepared according to a literature procedure.<sup>18</sup>

Dichloromethane was purified by refluxing the commercial product over calcium hydride, followed by distillation. Immediately before use, it was distilled over P<sub>2</sub>O<sub>5</sub>. Acetonitrile was purified by stirring overnight with calcium hydride, followed by distillation over fresh calcium hydride. Also this solvent was distilled over P<sub>2</sub>O<sub>5</sub> immediately before use. Dimethyl formamide (DMF), Fluka spectrograde, was dried 48 h over 4 Å molecular sieves, then distilled at 0.5 mm Hg from calcium hydride.

The cyclic voltammograms were obtained on platinum button electrodes in a three-compartment cell with an instrument constructed at the Chemistry Center of the University of Lund. It consisted of a potentiostat connected to a sweep generator. The voltammograms were recorded on a Watanabe X-Y recorder.

The ionic medium was 0.1 M Bu<sub>4</sub>NBF<sub>4</sub> in acetonitrile or dichloromethane. The reference electrode was an Ag|AgCl electrode from Metrohm, immersed in 0.1 M LiCl(aq). The nominal potential of this electrode is +0.280 V on the normal hydrogen scale at 20 °C and +0.0385 V against the saturated KCl calomel electrode (SCE).<sup>19</sup> In order to check the potential of the electrode in our system, voltammograms of 9,10-diphenylanthracene (DPA), which is known to undergo a reversible one-electron oxidation on platinum at +1.23 V (*vs.* SCE) in CH<sub>3</sub>CN (0.1 M Bu<sub>4</sub>N BF<sub>4</sub>)<sup>20a</sup> and at +1.22 V (*vs.* SCE) in CH<sub>2</sub>Cl<sub>2</sub> (0.2 M Bu<sub>4</sub>N ClO<sub>4</sub>)<sup>20b</sup> were run. In our hands DPA was reversibly oxidized with an anodic-cathodic peak separation of 90 mV. In CH<sub>3</sub>CN, the first anodic peak appeared at +1.20 V

(vs. Ag|AgCl), a value which compares well with the cited literature value. However, in CH<sub>2</sub>Cl<sub>2</sub> the first anodic peak appeared at +1.28 V (vs. Ag|AgCl), 100 mV more anodic than the cited literature value. This difference may be due to the lack of iR compensation in our apparatus and to liquid junction potentials.

The electrolyses were performed in a divided cell where the anode and cathode compartments were separated by a fritted glass disc. A stabilized power supply (Oltronix B504D) was used. The reference half cell (Metrohm, Ag|AgCl) was connected to the cell via a bridge, equipped with a fritted glass disc and filled with 0.1 M Bu<sub>4</sub>NBF<sub>4</sub> in dichloromethane or acetonitrile. Platinum electrodes were used.

IR-spectra were recorded on a Perkin Elmer 257 spectrometer, NMR spectra on a Varian EM-360 and GC-MS on a Finnegan 4021 instrument.

GC were run on a Varian Aerograph 1400 or a Carlo Erba Fractovap 2350, using stationary phases consisting of 7.5% SE 30 on Chromosorb for the determination of phenyl acetate and biphenyl and Chromosorb 102 for methane, ethane, bromomethane and methanol.

*Preparation of the cuprates* 4. Dry, purified copper (I) bromide<sup>21</sup> (0.072 g, 0.5 mmol) was suspended in dry THF (1 cm<sup>3</sup>) at -70 °C. On addition of phenyl lithium in benzene-ether (0.58 cm<sup>3</sup>, 0.5 mmol) a light yellow precipitate of phenyl copper was formed.<sup>22</sup> The appropriate amount of the nucleophile (acetate, sodium phenolate and the anions of dimethyl malonate and acetophenone) in in DMF (2 cm<sup>3</sup>) was added and the solution thus formed was used for the oxidation experiments.

*Electrochemical oxidation of compounds 1-3.* Compounds 1-3 were oxidized as summarized in Table 2. After oxidation, two different work-up procedures were used. In the first, the solvent and the volatile products were distilled into a cooled receiver and analyzed by GLC.

In the second procedure, the ionic medium was precipitated by addition of diethyl ether and the filtrate analyzed by GC.

*Oxidation of compounds 4.* Compounds 4, prepared *in situ* as described above, were oxidized as summarized in Table 3, either chemically with air or electrochemically. The yields of the compounds were determined by GLC, using 1,2-diphenylethane as internal standard.

*Acknowledgements.* This paper is submitted in honor of Professor Holger Erdtman on the occasion of his 80th birthday in appreciation of his contributions to organic chemistry. We thank the Swedish Natural Science Research Council and the French CNRS for financial support.

## REFERENCES

- Participant in the exchange between CNRS (France) and NFR (Sweden). Permanent address: Laboratoire de chimie organometallique, Université Paris XIII, Av. J. B. Clement, 93430 Villetaneuse, France.
- a. Parshall, G. W. *The Homogenous Catalytic Activation of C-H Bonds*, Catalysis, Vol. 1. Specialist Periodical Report, Kemball, C. senior reporter, The Chemical Society, London 1977, p. 335; b. Shilov, A. E. and Shteinman, A. A. *Coord. Chem. Rev.* 24 (1977) 97; c. Webster, O. *Adv. Organomet. Chem.* 15 (1977) 147; d. Ittel, S. D., Tolman, C. A., English, A. D. and Jesson, J. P. *J. Am. Chem. Soc.* 100 (1978) 7577; e. Remick, R. J., Asunta, T. A. and Skell, P. S. *Ibid.* 101 (1979) 1320; f. Billups, W. E., Konarski, M. M., Hauge, R. H. and Margrave, J. L. *J. Am. Chem. Soc.* 102 (1980) 7393; g. Ozin, G. A., McIntosh, D. F. and Mitchell, S. A. *Ibid.* 103 (1981) 1574.
- a. Dodd, D. and Johnson, M. D. *J. Organomet. Chem.* 52 (1973) 1; b. Anderson, S. N., Ballard, D. H., Chrzastowski, J. Z., Dodd, D. and Johnson, M. D. *J. Chem. Soc. Chem. Commun.* (1972) 685; c. Bäckvall, J.-E. *Tetrahedron Lett.* (1975) 2225; d. Bäckvall, J.-E. *Ibid.* (1977) 467; e. Halpern, J., Chan, M. S., Hanson, J., Roche, T. S. and Topich, J. A. *J. Am. Chem. Soc.* 97 (1975) 1606; f. Levitin, I. YA, Sigan, A. L. and Volpin, M. E. *J. Organomet. Chem.* 114 (1976) C53; g. Magnuson, R. H., Halpern, J., Levitin, I. Ya and Volpin, M. E. *J. Chem. Soc. Chem. Commun.* (1978) 44; h. Abis, L., Sen, A. and Halpern, J. *J. Am. Chem. Soc.* 100 (1978) 2915.
- a. Wennerström, O. *Diss.*, Royal Institute of Technology, Stockholm 1971; b. Björklund, C. *Diss.*, Royal Institute of Technology, Stockholm 1972; c. Lewin, A. H. and Goldberg, N. L. *Tetrahedron Lett.* (1972) 491; d. Cohen, T., Wood, J. and Dietz, A. G. *Ibid.* (1974) 3555.
- a. Tsou, T. T. and Kochi, J. *J. Am. Chem. Soc.* 100 (1978) 1634; b. Almemark, M. and Åkermark, B. *J. Chem. Soc. Chem. Commun.* (1978) 66.
- Åkermark, B. and Ljungquist, A. *J. Organomet. Chem.* 182 (1979) 59.
- Jönsson, L. *Acta Chem. Scand. B* 34 (1980) 697.
- Bäckvall, J.-E. and Nordberg, R. E. *J. Am. Chem. Soc.* 102 (1980) 393.
- a. Semmelhack, M. F. *J. Organomet. Chem. Libr.* 1 (1976) 361; b. Ebersson, L., Jönsson, L. Wistrand, L.-G. *Tetrahedron Report. In press.*
- a. Nilsson, M. *Acta Chem. Scand.* 12 (1958) 537; b. Hardy, W. B. and Fortenbaugh, J. *J. Am. Chem. Soc.* 80 (1958) 1716; c. van Koten, G., Jastrzebski, J. T. B. H. and Noltes, J. G. *Tetrahedron Lett.* (1976) 223.

11. Bäckvall, J.-E., Åkermark, B. and Ljunggren, S.-O. *J. Am. Chem. Soc.* 101 (1979) 2411.
12. a. Ebersson, L. *Adv. Phys. Org. Chem.* 18 (1981) 79; b. Wasielewski, M. R. and Breslow, R. *J. Am. Chem. Soc.* 98 (1976) 4222.
13. Latimer, W. M. and Hildebrand, J. H. *Reference Book of Inorganic Chemistry*, Macmillan, New York 1951, p. 529.
14. a. Kharasch, M. S. and Sosnovsky, G. *Tetrahedron* 3 (1958) 105; b. Kochi, J. *Tetrahedron* 18 (1962) 483; c. Kochi, J. In Kochi J., Ed., *Free Radicals*, Wiley-Interscience, New York 1973, p. 591.
15. a. King, R. B. *Inorg. Chem.* 5 (1966) 82; b. Yamazaki, H. and Hagiharu, W. *J. Organomet. Chem.* 21 (1970) 431.
16. Costa, G., Mestroni, G. and Tauzher, G. *J. Chem. Soc. Dalton Trans.* (1972) 450.
17. Farmery, K. and Busch, D. H. *Inorg. Chem.* 11 (1972) 2901.
18. Steigman, J. and Lorentz, P. M. *J. Am. Chem. Soc.* 88 (1966) 2093.
19. Weast, R. O. *Handbook of Chemistry and Physics*, The Chemical Rubber Co., 55th Ed., 1974, p. D-120.
20. a. Hammerich, O. and Parker, V. D. *J. Am. Chem. Soc.* 96 (1974) 4289; b. Phelps, J., Santhanam, K. S. V. and Bard, A. J. *J. Am. Chem. Soc.* 89 (1967) 1752.
21. Kauffman, G. B. and Teter, L. A. *Inorg. Synth.* 7 (1963) 9.
22. Costa, G., Camus, A., Marsick, N. and Gatti, L. *J. Organomet. Chem.* 5 (1966) 568.

Received November 16, 1982.