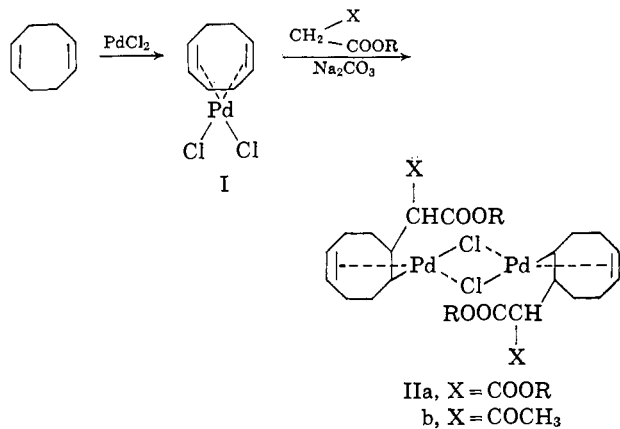


philes such as amines<sup>3</sup> and acetate anion<sup>4</sup> with olefin-palladium chloride complexes have also been reported. Consideration of these reactions leads us to undertake a study of reactions of these complexes with carbanions, since no attempt has been made as yet to study the nucleophilic attack of carbanions on the complex.

We at first selected the 1,5-cyclooctadiene-palladium chloride complex (I). When the complex I was treated with an excess of ethyl malonate in the presence of sodium carbonate at room temperature, the yellow complex gradually turned whitish, indicating the formation of a new complex. The new complex was recrystallized from ethyl acetate. By analogy with  $\mu, \mu$ -dichlorobis(8-methoxy-4-cyclooctenyl)dipalladium,<sup>5</sup> we propose that the new complex has the structure  $\mu, \mu$ -dichlorobis(8-dicarbethoxymethyl-4-cyclooctenyl)dipalladium (IIa), m.p. 155–156°. *Anal.* Calcd. for  $(C_{15}H_{23}O_4PdCl)_2$ : C, 43.99; H, 5.66; Cl, 8.66; Pd, 26.0. Found: C, 43.84; H, 5.70; Cl, 8.73; ash, 25.3. Ethyl acetoacetate behaved in the same way giving the complex IIb, m.p. 157–158°. *Anal.* Calcd. for  $(C_{14}H_{21}O_3PdCl)_2$ : C, 44.31; H, 5.57; Cl, 9.34; Pd, 28.1. Found: C, 44.23; H, 5.49; Cl, 9.36; ash, 27.8. For a complete structure determination, an X-ray crystallographic study is in progress.

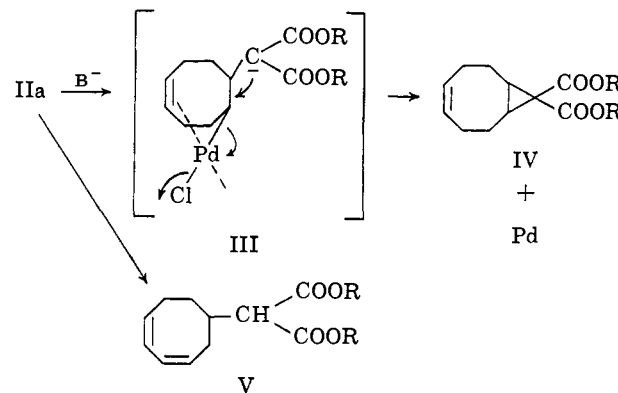


Decomposition of the complex IIa with base was then studied. The addition of methylsulfinyl carbanion<sup>6</sup> to a dimethyl sulfoxide solution of the complex IIa gave a substituted malonate anion (III), which in turn attacked the carbon  $\sigma$ -bonded to the palladium, giving rise to metallic palladium and diethyl bicyclo[6.1.0]non-4-ene-9,9-dicarboxylate (IV), b.p. 120° (bath temperature) (0.2 mm.), which was converted to bicyclo[6.1.0]nonane-9,9-dicarboxylic acid by hydrogenation and hydrolysis; m.p. 208–209°, undepressed with an authentic sample prepared by the reaction of cyclooctene with ethyl diazomalonate,<sup>7</sup> followed by hydrolysis. *Anal.* Calcd. for  $C_{11}H_{16}O_4$ : C, 62.31; H, 7.61. Found: C, 62.50; H, 7.55.

On the other hand, the attack of weaker bases such as trimethylamine or sodium carbonate in boiling benzene induced a simple decomposition of the complex IIa, giving ethyl 3,5-cyclooctadienylmalonate (V). *Anal.* Calcd. for  $C_{15}H_{22}O_4$ : C, 67.64; H,

8.33; mol. wt., 266. Found: C, 67.48; H, 8.31; mol. wt., 266 (mass spectroscopy). The positions of the double bonds were determined by ultraviolet [ $\lambda_{max}^{MeOH}$  229 m $\mu$  ( $\epsilon$  4900)] and n.m.r. spectra. Hydrogenation followed by hydrolysis gave cyclooctylmalonic acid; m.p. 123–124°, undepressed with an authentic sample. *Anal.* Calcd. for  $C_{11}H_{16}O_4$ : C, 61.66; H, 8.47. Found: C, 61.58; H, 8.38.

Thus, these reactions show not only a facile nucleophilic attack of carbanions on the palladium chloride complex, but also new methods of formation of cyclopropanes and of carbon to carbon bonds. The



reaction of various palladium chloride complexes with carbanions will be reported in a forthcoming paper.

Jiro Tsuji, Hidetaka Takahashi  
Basic Research Laboratories  
Toyo Rayon Co., Ltd., Kamakura, Japan  
Received April 29, 1965

### Alkyl-lithium–Amine Crystalline Complexes

*Sir:*

From previous studies of solution properties, we proposed that lithium alkyls (RLi) can form specific coordination complexes containing neutral Lewis bases (B), e.g., ethers and *t*-amines, with a 1:2 base:lithium ratio ( $R_2Li_2 \cdot B$ ).<sup>1,2</sup> We have now isolated crystalline complexes of the lithium alkyls and characterized them as containing the 1 base unit/pair of lithium atoms.

In the earlier work, solution properties had indicated that steric requirements of the base were important to the complexation and, hence, using a cyclic ether like tetrahydrofuran could be more efficacious than using the more basic triethylamine (I).<sup>1c</sup> Comparison of the solution properties using several amines of lower steric requirements, primarily methylamines and cyclic amines, has revealed that quinuclidine(II) is particularly effective in complexing lithium alkyls, just as this base is particularly effective in complexing trimethylboron.<sup>3</sup> For example, although I shows no interaction with the *t*-butyllithium reagent,<sup>1c</sup> II precipitates this bulky reagent from solution. Several amine–lithium reagent complexes are relatively insoluble, but by far the least soluble are those with the dibasic triethylenediamine, TED (III).<sup>4</sup> By an-

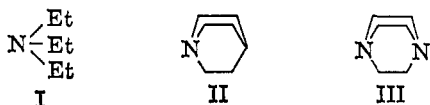
(3) E. W. Stern and M. L. Spector, *Proc. Chem. Soc.*, 370 (1961).  
 (4) I. I. Moiseev, M. N. Vargaftik, and Ya. K. Syrkin, *Dokl. Akad. Nauk SSSR*, 133, 377 (1960).  
 (5) J. Chatt, L. M. Vallarino, and L. M. Venanzi, *J. Chem. Soc.*, 3413 (1957).  
 (6) E. J. Corey and N. Chaykovsky, *J. Am. Chem. Soc.*, 84, 866 (1962).  
 (7) H. Musso and U. Biethan, *Chem. Ber.*, 97, 2282 (1964).

(1) (a) J. F. Eastham and G. W. Gibson, *J. Am. Chem. Soc.*, 85, 2171 (1963); (b) Z. K. Cheema, G. W. Gibson, and J. F. Eastham, *ibid.*, 85, 3517 (1963); (c) F. A. Settle, M. Haggerty, and J. F. Eastham, *ibid.*, 86, 2076 (1964).

(2) Solution properties of a lithium alkyl–amine system have also been studied by T. L. Brown, R. L. Geteis, D. A. Bafus, and J. A. Ladd, *ibid.*, 86, 2135 (1964).

(3) H. C. Brown and S. Sujishi, *ibid.*, 70, 2871 (1948).

alogy to the 1:2 base:lithium ratio found earlier, complexes formed with the dibasic species III were anticipated to have an empirical formula with 4 alkyl lithium units/TED unit, *i.e.*,  $R_2Li_2$ -TED- $R_2Li_2$ .



Thus we have found that when it is added to solutions of organolithium reagents, TED forms crystalline precipitates with every reagent tested, which include those with organic groups of methyl, ethyl, *n*-butyl, *t*-butyl, phenyl, 2-thienyl, benzyl, and 9-fluorenyl, making possible the isolation and characterization of the complex.<sup>5</sup> In most cases *addition of just 0.25 mole of TED/g.-atom of lithium causes quantitative precipitation of the organometallic reagent*, and analysis of the crystalline product agrees with the anticipated empirical formula.<sup>6</sup> Formation of 1:4 complexes with the aryllithium reagents, phenyl and 2-thienyl, seems particularly interesting.

Only in the two cases of benzyl- and 9-fluorenyllithium did the complexes which precipitated contain 1 mole of the TED/organolithium unit. Formation of a 1:1 complex in just these two cases most likely was because only in these cases could the organic group exist as a carbanion stabilized by benzyl-type charge delocalization. The benzyl- and 9-fluorenyllithium reagents are similarly distinguished by their formation of insoluble complexes with triethylamine; the complexes of other lithium reagents with triethylamine are quite soluble.<sup>10,2</sup>

For lithium reagents, most of which are liquids when pure, the amine complexes constitute the first general, nondestructive technique for obtaining crystalline derivatives; these derivatives can be conveniently used in conventional reactions of the lithium reagents, in some cases with exceptional results (*vide infra*). Some preliminary observations have been made in applications of TED to the complexation of other organometallics. No mercury, boron, or aluminum alkyl solutions we have examined form precipitates when the amine is added. However, Grignard reagents do form crystalline complexes with TED and, similarly, dialkylmagnesium reagents are precipitated, even from dioxane solution. Diethylzinc also is readily precipitated by TED. The stoichiometry of formation of these new complexes will be reported subsequently.

Base catalysis of reactions of lithium alkyls is striking, particularly for metalation.<sup>7</sup> For example, although thiophene in hexane solution does not react with butyllithium alone, 2-thienyllithium is rapidly

(4) Use of a diamine was suggested by our previous observation<sup>10</sup> that dioxane, an oxygen analog of III, formed an insoluble complex with butyllithium, but the complex was so reactive as to be difficult to characterize with assurance.

(5) A benzene solution of TED was normally added to a solution of lithium reagent in hydrocarbon solvent, but in the case of methyl- and phenyllithium, ether was present.

(6) The stoichiometry of the 1:4 TED-alkyllithium complexes has been determined both by analysis of the amount of organometallic left in standard solutions after precipitation with known quantities of TED and by potentiometric titration of the hydrolysate of the isolated complexes themselves. Further, hydrolyses of the complexes have been shown to yield TED and the expected hydrocarbons, and carbonation to yield the expected carboxylic acids.

(7) W. A. Butte (*J. Org. Chem.*, **29**, 2928 (1964)) has also observed this striking catalysis of metalation, particularly using amines capable of chelation.

and essentially quantitatively formed if 0.5 mole equiv. of triethylamine is present. Hydrocarbon aromatics, particularly benzene and its homologs, are more difficult to metalate and have been generally resistant to this reaction with lithium alkyls in ethereal solvents.<sup>8</sup> Such metalations can now be conveniently effected by catalysis with one of the sterically less demanding *t*-amines. Thus conversion of toluene to benzyl lithium by a lithium alkyl is easily promoted by II, III, or trimethylamine; *e.g.*, with a 0.1 *M* solution of the latter in toluene containing *sec*-butyllithium, standing overnight at room temperature followed by carbonation gives a 75% yield of pure phenylacetic acid. In many respects amine catalysis makes the lithium alkyls react like the generally more active sodium and potassium alkyls. In this manner phenyllithium can be used to prepare benzyl lithium from toluene, which is akin to the standard preparation of benzylsodium from phenylsodium.<sup>9</sup> The alkyl lithium-amine reaction metalates *t*-butylbenzene on the ring, which is also a metalation previously accomplished only with sodium and potassium alkyls.<sup>10</sup> Refluxing benzene itself with butyllithium-triethylenediamine followed by carbonation produces benzoic acid in essentially quantitative yield.

It appears that those attributes which make an amine a particularly effective complexing agent also make that amine a particularly effective reaction catalyst, but it is not clear whether these two things are coincidental or are consequential. We are convinced though that low steric requirements of a neutral base is a prime attribute for both effects.

**Acknowledgment.** This research was made possible by Contract AT-(40-1)-1983 between the University of Tennessee and the U. S. Atomic Energy Commission.

(8) As a leading reference to earlier attempts to use lithium alkyls to metalate such hydrocarbons as benzene and toluene, see H. Gilman and J. W. Morton, *Org. Reactions*, **8**, 265, 290 (1954), and H. Gilman and B. J. Graj, *J. Org. Chem.*, **28**, 1725 (1963).

(9) J. F. Nobis and L. F. Moormier, *Ind. Eng. Chem.*, **46**, 539 (1954).

(10) Cf. R. A. Benkeser, D. J. Foster, and D. M. Sauve, *Chem. Rev.*, **57**, 867 (1957); R. A. Benkeser, Abstracts of Papers, 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., September 1962, p. 4Q.

Constantinos G. Screttas, Jerome F. Eastham

Department of Chemistry, The University of Tennessee  
Knoxville, Tennessee

Received February 10, 1965

## Reductive Coupling of Alcohols to Hydrocarbons

Sir:

By means of experiments presupposing the valence change  $II \rightarrow IV$  for an appropriate metal, we have been able to effect, in a single laboratory operation, the heretofore unknown reductive coupling of an alcohol (ROH) to a hydrocarbon (R-R). Experiments were designed in accordance with eq. 1,<sup>1</sup> which represents a reduction principle (2) of potentially broader utility in



the field of synthetic organic chemistry.

(1) Although there is formal analogy between the titanium (II) alkoxide structure and that of acyclic dialkoxy-carbenes (RO-C-OR), the latter apparently do not lose carbon dioxide, but instead give rise to diverse other products: R. W. Hoffmann and H. Häuser, *Tetrahedron Letters*, 197 (1964); D. M. Lemal, E. P. Gossélink, and A. Ault, *ibid.*, 579 (1964).