

the facile addition of the alkyl halide gases where formation of ion intermediates can be excluded.

A one-step addition would require retention of configuration at the carbon atom. This has been confirmed by the addition and subsequent cleavage of optically active $\text{CH}_3\text{CHBrCOOC}_2\text{H}_5$. The regenerated bromoester has the same sign of rotation as the original. Thus two inversions or two retentions must be involved. Cleavage of alkyl-metal bonds with Br_2 is known to almost entirely occur with retention.⁸ Thus the oxidative addition must also go with retention. In this case, however, because of the complexity of the ir spectrum, we were not able to decide if the addition was cis or trans.

A one-step addition of silicon hydrides to d^8 complexes has also been postulated.⁹ In agreement with our work, Sommer has shown¹⁰ that addition of silicon hydrides to $\text{Ir}(\text{CO})\text{Cl}[\text{P}(\text{C}_6\text{H}_5)_3]_2$ occurs with retention of configuration at silicon.

Orbital symmetry considerations do not exclude a two-step mechanism for the reaction of d^8 complexes with alkyl halides (Figure 1c). A possible example, which goes with inversion of configuration at carbon, has been reported.¹¹

Acknowledgment. The authors wish to acknowledge the valuable help of R. W. Johnson. Financial support came from the Atomic Energy Commission, Grant No. AT(11-1)-1087, and from a predoctoral NIH fellowship for W. R. M.

(8) F. R. Jensen and L. H. Gale, *J. Amer. Chem. Soc.*, **82**, 148 (1960); F. R. Jensen, L. D. Whipple, D. K. Wedegaertner, and J. A. Landgrebe, *ibid.*, **82**, 2466 (1960). R. W. Johnson (private communication) has shown that bromine cleavage of $\text{CH}_3\text{CHCOOC}_2\text{H}_5\text{Mn}(\text{CO})_5$ occurs with retention of configuration.

(9) J. F. Harrod and C. A. Smith, *J. Amer. Chem. Soc.*, **92**, 2699 (1970).

(10) L. H. Sommer, J. E. Lyons, and H. Fujimoto, *ibid.*, **91**, 7051 (1969).

(11) J. A. Labinger, R. J. Braus, D. Dolphin, and J. A. Osborn, *Chem. Commun.*, 612 (1970).

(12) Address correspondence to this author.

Ralph G. Pearson,¹² Warren R. Muir

Department of Chemistry, Northwestern University
Evanston, Illinois 60201

Received June 23, 1970

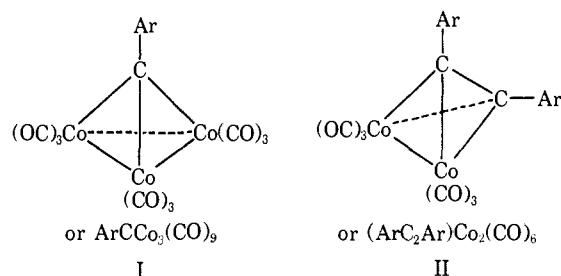
Aromatic Electrophilic Substitution Reactions of Phenylmethylidynetricobalt Nonacarbonyl and Diphenylacetylenedicobalt Hexacarbonyl. Preparatively Useful Reactions of Coordinated Organic Ligands

Sir:

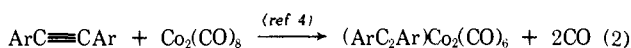
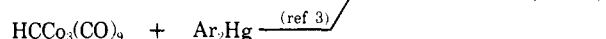
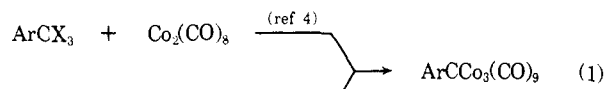
Electrophilic substitution reactions of π -bonded unsaturated organic ligands in transition metal complexes are well known¹ and such reactions can be valuable in organic synthesis when procedures are available for subsequent release of the organic ligand from the com-

(1) Some examples: (a) π -bonded cyclobutadiene in $\pi\text{-C}_4\text{H}_4\text{Fe}(\text{CO})_5$: J. D. Fitzpatrick, L. Watts, G. F. Emerson, and R. Pettit, *J. Amer. Chem. Soc.*, **87**, 3254 (1965); (b) π -bonded cyclopentadienyl in ferrocene: R. B. Woodward, M. Rosenblum, and M. C. Whiting, *ibid.*, **74**, 3458 (1952); (c) π -bonded benzene in benzene-chromium tricarbonyl: R. Ercoli, F. Calderazzo, and E. Mantica, *Chim. Ind. (Milan)*, **41**, 404 (1959); R. Riemschneider, O. Becker, and K. Franz, *Monatsh. Chem.*, **90**, 571 (1959); (d) π -bonded cycloheptatriene and cyclooctatetraene in their iron tricarbonyl complexes: B. F. G. Johnson, J. Lewis, and G. L. P. Randall, *Chem. Commun.*, 1273 (1969); B. F. G. Johnson, J. Lewis, A. W. Parkins, and G. L. P. Randall, *ibid.*, 595 (1969).

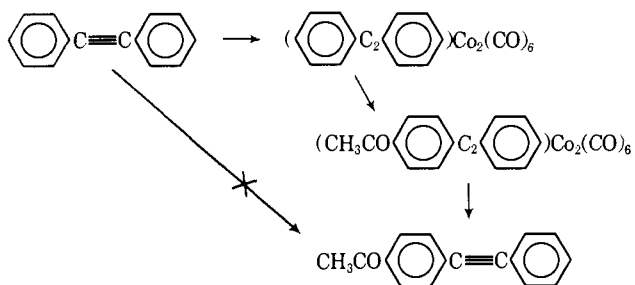
plex.^{1a} Through our recent research in the area of carbon-cobalt cluster compounds,^{2,3} we became interested in the possibility of organic transformations involving the ligands in compounds of types I and II.



Both types of complexes are quite stable and easily prepared and handled (eq 1 and 2).⁴



We have found that compounds of types I and II where Ar = phenyl undergo facile Friedel-Crafts acylation and that the organic ligands in the resulting products can be released from their cobalt complexes to give organic compounds in high yield. Such a reaction sequence is of special interest and utility in the case of $(\text{PhC}_2\text{Ph})\text{Co}_2(\text{CO})_6$ since Friedel-Crafts acylation of the free ligand, diphenylacetylene, cannot be accomplished directly. Both types of complexes, I and II, were found



to be stable to the conditions of the Friedel-Crafts reaction and we have introduced acetyl, benzoyl, and formyl substituents in this manner (Schemes I and II).

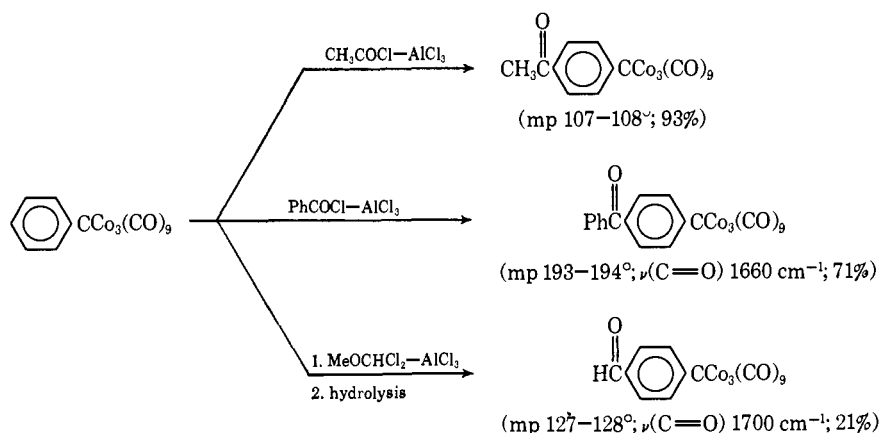
The acetylation of phenylmethylidynetricobalt nonacarbonyl is described to illustrate the procedure used. A slurry of 5 mmol of anhydrous AlCl_3 in 50 ml of dichloromethane under argon was cooled to 0° and 5 mmol of acetyl chloride was added. The mixture was stirred at 0° for 10 min and then 5 mmol of $\text{PhCCo}_3(\text{CO})_9$ in 50 ml of dichloromethane was added. The reaction mixture was stirred at 0° for 15 min, at 25° for 2 hr, and subsequently poured onto ice water. Extraction of the aqueous phase was followed by drying and evaporation of the solvent. Low-temperature crystallization of the residue from hexane gave 2.6 g (93%) of brown-black solid, mp $106\text{--}107^\circ$. A sample recrystal-

(2) D. Seyferth, R. J. Spohn, M. R. Churchill, K. Gold, and F. R. Scholer, *J. Organometal. Chem.*, **23**, 237 (1970).

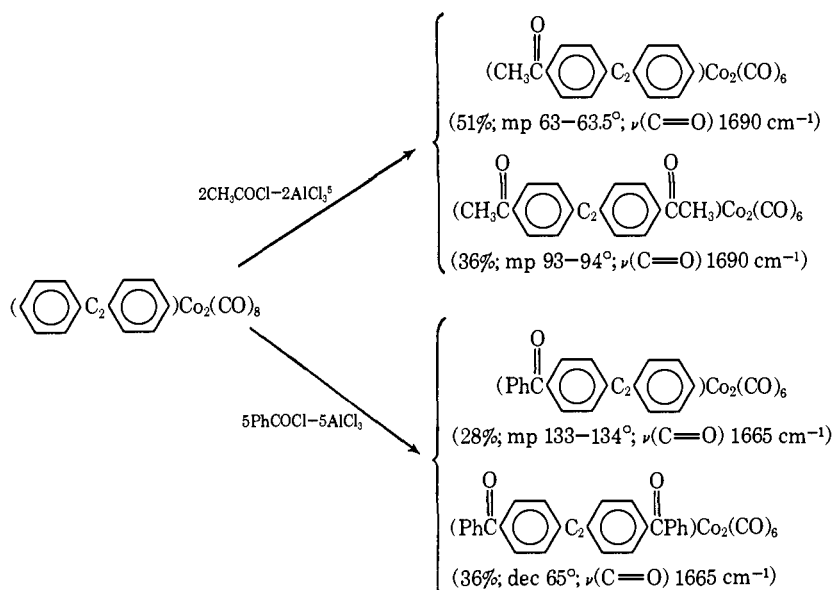
(3) D. Seyferth, J. E. Hallgren, and R. J. Spohn, *ibid.*, in press.

(4) W. Hübel in "Organic Syntheses via Metal Carbonyls," Vol. 1, I. Wender and P. Pino, Ed., Interscience, New York, N. Y., 1968, pp 273-342.

Scheme I



Scheme II



lized from hexane, mp 107–108°, analyzed correctly for $C_{18}H_{7}O_{10}Co_3$. Its infrared spectrum (CCl_4) showed bands at 2100, 2050, 2040, 2020, 1685 ($C=O$), 1590, 1390, 1310, 1270, 1260, 955, 910, and 675 cm^{-1} ; its nmr spectrum ($CDCl_3$) showed a singlet at δ 2.55 (CH_3) and two doublets at 7.4 and 7.9 ppm ($J = 8$ Hz for both). Thus, acetylation in the para position seems indicated.⁶

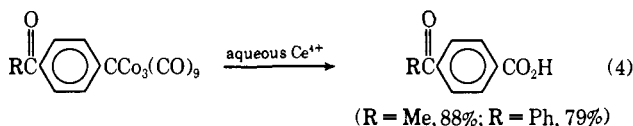
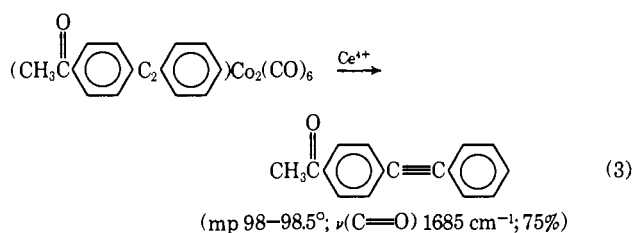
Release of the organic ligands from these cobalt carbonyl complexes is easily accomplished with ceric ammonium nitrate in acetone. Such oxidation of the $(ArC_2Ar)Co_2(CO)_6$ compounds regenerates the acetylene in high yield (eq 3).⁷ Prepared in similar fashion were bis(*p*-acetylphenyl)acetylene (72%, mp 198.5–200°, $\nu(C=O)$ 1680 cm^{-1}), *p*-benzoylphenyl(phenyl)acetylene (58%; mp 110–111.5°; $\nu(C=O)$ 1655 cm^{-1}), and bis(*p*-benzoylphenyl)acetylene (80%; mp 226–227.5°; $\nu(C=O)$ 1655 cm^{-1}). The action of ceric ammonium nitrate in aqueous acetone solution on the $ArCCO_3(CO)_9$ compounds gave the corresponding carboxylic acids,

(5) A reagent ratio of $5CH_3COCl + 5AlCl_3 + (PhC_2Ph)Co_2(CO)_6$ gave only the diacetylated product in 62% yield.

(6) The nmr spectrum (DMSO) of $(CH_3COC_6H_4C_2C_6H_4COCH_3)Co_2(CO)_6$ also indicated that acetylation had occurred mostly, if not exclusively, in the para position: δ 2.6 (s, 6, CH_3), 7.1 (d, 2, $J = 8$ Hz), 7.6 ppm (d, 2, $J = 8$ Hz).

(7) This reaction was discovered in these laboratories by Dr. D. L. White in connection with another project.

$ArCO_2H$, in good yield (eq 4). Both of these acids (as the crude products) were converted to their methyl



esters with ethereal diazomethane. It was established by comparison with authentic samples (ir, glc,⁸ and mixture melting point) that in each case *only* the para isomer was present. This supports the nmr evidence which spoke for para substitution in $CH_3COC_6H_4-CCO_3(CO)_9$. The nature of the factors which determine directive effects in the electrophilic aromatic substitu-

(8) DC-200 column at 190° for the acetyl compound, UCW98 column at 215° for the benzoyl compound. The esters, being solids of mp 95 and 107°, respectively, were injected as DMF solutions.

tion reactions of complexes of types I and II is under investigation.

It was known that $\text{RCCo}_3(\text{CO})_9$ compounds are degraded to RCBr_3 by bromine in carbon tetrachloride,⁹ and thus it was not surprising that treatment of I and II ($\text{Ar} = \text{Ph}$) with electrophilic reagents which also are oxidizing agents (*e.g.*, nitric-sulfuric mixed acid, acetyl nitrate, nitronium tetrafluoroborate, 30% oleum, etc.) caused massive decomposition. However, treatment of $\text{PhCCo}_3(\text{CO})_9$ with bromine in methanol followed by basic (10% aqueous NaOH) hydrolysis of the reaction product gave benzoic acid in 80% yield, and thus an alternate scheme for the degradation of such complexes is available.

Satisfactory carbon and hydrogen analyses ($\pm 0.3\%$) were obtained for all new compounds prepared in this study. Our investigations in this area are continuing.

Acknowledgments. The authors are grateful to the National Science Foundation (Grant NSF 6466X) for generous support of this work. This research was supported in part by Public Health Service Fellowship 1-FO2-CA43388-01 (to A. T. W.).

(9) U. Krüerke and W. Hübel, *Chem. Ind. (London)*, 1264 (1959).
* To whom correspondence should be addressed.

Dietmar Seyferth,* Anthony T. Wehman

Department of Chemistry, Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received June 29, 1970

A Method for the Introduction of Two Carbon Appendages at a Carbonyl Carbon. Application to Double Chain Branching and Spiro Annulation Operations

Sir,

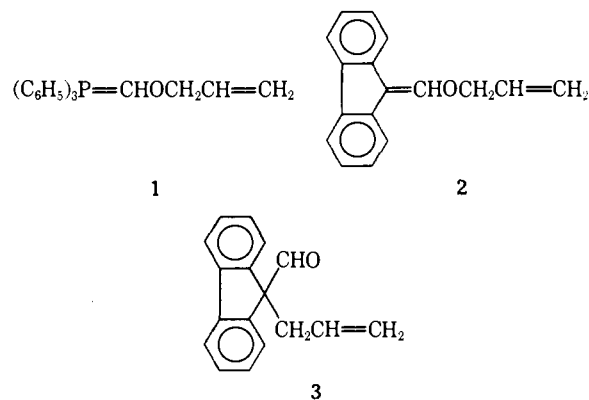
This communication reports a general two-step sequence for the replacement of carbonyl oxygen by two functionalized carbon substituents which can be elaborated to form rings or more complex chains. The process leads to the formation of spiro ring systems in a novel and quite flexible way starting from a cyclic ketone and to the introduction of a pair of branches starting from an acyclic ketone. Two modifications of the method will be described, one being applicable to aryl conjugated ketones and the other to nonconjugated ketones.

Treatment of allyloxymethyltriphenylphosphonium chloride (mp $136\text{--}138^\circ \text{dec}$)^{1,2} at -45° in 2:1 tetrahydrofuran (THF)-hexamethylphosphorotriamide³ with 1 equiv of *sec*-butyllithium in cyclohexane gave a red-brown solution containing the ylide 1, the formation of which was verified by reaction with fluorenone (-45° for 30 min, then 0° for 16 hr) to give the enol ether 2² in 62% yield. Thermolysis of 2 at 152° for 45 min afforded the doubly branched unsaturated aldehyde 3² (74% yield). This aldehyde is a useful intermediate for the generation of a variety of spiro systems by stand-

(1) Prepared from allyl chloromethyl ether [C. D. Hurd, L. G. Ginger, L. L. Gershbein, and W. A. Yarnall, *J. Amer. Chem. Soc.*, **74**, 5128 (1952)] and triphenylphosphine in acetonitrile.

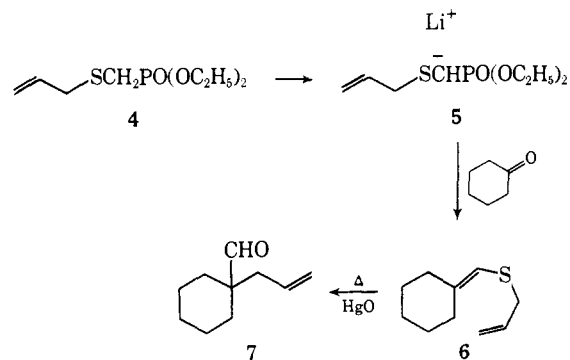
(2) This compound was characterized satisfactorily by (a) analytical and (b) spectroscopic (infrared and nuclear magnetic resonance) data.

(3) All Wittig reactions, all reactions involving organometallic reagents, and all thermal rearrangements were conducted under an atmosphere of argon.



ard synthetic operations such as are outlined below. In a similar way benzaldehyde was converted in a two-step branching sequence to 2-phenyl-4-pental² in 70% overall yield.

Although ylide 1 gave good yields of allyl enol ethers with aromatic aldehydes and ketones, no enol ethers could be obtained with alicyclic or enolizable ketones, *e.g.*, cyclohexanone, as substrates. Therefore, some modification was required to broaden the scope of the branching-annulation sequence. Toward this end, diethyl allylthiomethylphosphonate, 4,² bp $77\text{--}78^\circ$ (0.11 mm), was prepared in 67% yield by the Arbuzov reaction of triethyl phosphite and allyl chloromethyl sulfide.⁴ Slow addition⁵ of *sec*-butyllithium in cyclohexane to a THF solution of 4 at -78° afforded the anion 5, which upon reaction with cyclohexanone (30 min at -78° , warming to 25° over 15 min, then 15 hr at 50°) gave the allyl vinyl sulfide 6.^{2,6} Heating 6 at $160\text{--}180^\circ$



afforded only starting material and intractable tars; this was not unexpected, since thioaldehydes polymerize quite readily.⁷ However, when 6 was heated at 190° for 10 min in the presence of 3 equiv of red mercuric oxide, 1-allyl-1-cyclohexancarboxaldehyde (7),^{2,8} could be obtained in 82% yield by distillation from the black residue of HgS-HgO . This result supports the working hypothesis that mercuric oxide might promote the rapid conversion of an intermediate thioaldehyde to the corresponding aldehyde and thereby exclude complex side

(4) L. A. Walter, L. H. Goodson, and R. J. Fosbinder, *J. Amer. Chem. Soc.*, **67**, 655 (1945).

(5) Faster than dropwise addition caused localized heating and decomposition of the phosphonate anion.

(6) For a report on the application of lithium reagents from (1-methylthio)alkylphosphonate esters to the synthesis of vinyl sulfides and ketones, see E. J. Corey and J. I. Shulman, *J. Org. Chem.*, **35**, 777 (1970).

(7) E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. III, Chemical Publishing Co., New York, N. Y., 1960, p 148.

(8) Mp of 2,4-DNP, $153\text{--}154^\circ$ [lit. mp $156\text{--}157^\circ$; see K. C. Brannock, *J. Amer. Chem. Soc.*, **81**, 3379 (1959)].