Tetrahedron Letters No. 48, pp 4163 - 4166, 1977. Pergamon Press. Printed in Great Britain.

TRANSITION METAL-STABILIZED CARBENIUM IONS AS SYNTHETIC INTERMEDIATES. I.
α-[(ALKYNYL)DICOBALT HEXACARBONYL] CARBENIUM IONS AS PROPARGYLATING AGENTS

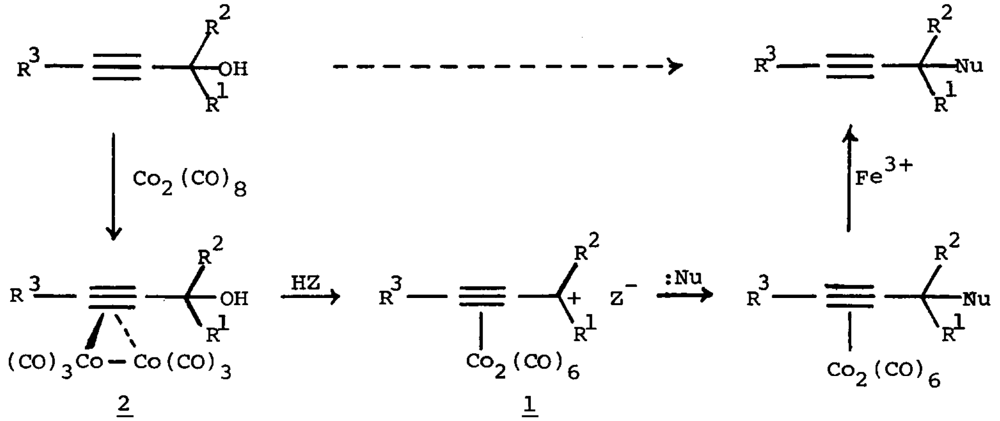
Rosa F. Lockwood and Kenneth M. Nicholas*
Department of Chemistry, Boston College,
Chestnut Hill, Mass. 02167

(Received in USA 22 August 1977; received in UK for publication 11 October 1977)

A phenomenon of long-standing interest in organometallic chemistry is the tremendously enhanced stability of carbenium ions flanked by organo-transition metal moieties.[1] While considerable attention has centered upon the magnitude and possible modes of this stabilization, the potential utility of these cations in organic synthesis has remained essentially unexplored.[2] As part of a program to address this question, we have been studying the chemistry of the cobalt-complexed cations 1. We now report reactions of complexes 1 with reactive aromatics which provide a flexible propargylation method for the generation of 2°, 3° and 4° centers.

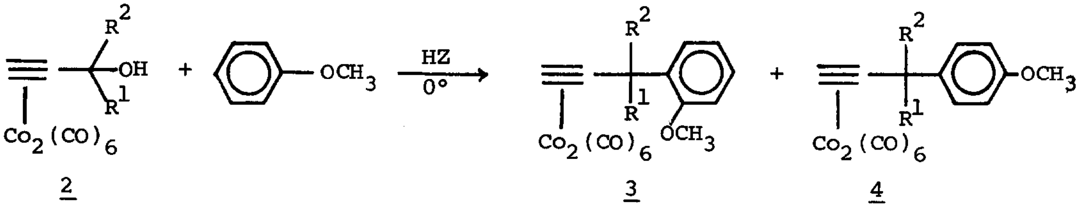
Earlier the stability of these cations was established by determining their pK_{R^+} values and by isolating and characterizing several of their salts.[3] Since the activating $-Co_2(CO)_6$ unit is introduced[4] and removed[5] efficiently and under mild conditions, these complexes appeared to be ideally suited for utilization as electrophilic propargyl synthons (Scheme 1).

Scheme 1



Dissolution of the cation salts 1a(R^1=R^2=R^3=H;Z=BF_4^-), 1b (R^1,R^3=H; R^2=CH_3;Z=BF_4^-) or, better, the complexed alcohols 2a, 2b or 2c (R^3=H;R^1=R^2=CH_3) and $HBF_4\cdot(CH_3)_2O$ in anisole at 0° results in a rapid reaction as indicated by

TLC analysis.[6] After evaporative removal of anisole and column chromatography, the product complexes were isolated in good yield (Table I) as dark red oils. Their IR and ^{1}H NMR spectra are in accord with structures 3a, 3b and 4a-c in



which the (propargyl)$Co_2(CO)_6$ unit has been introduced into the aromatic ring. The assigned structures were further supported by spectroscopic characterization (NMR, IR, MS) of the free ligands obtained after oxidative demetalation ($Fe(NO_3)_3 \cdot 9H_2O$/EtOH).[5a] The observed ortho/para product ratios appear to reflect the increasing steric bulk of the complexed cations in the series 1a→1c.

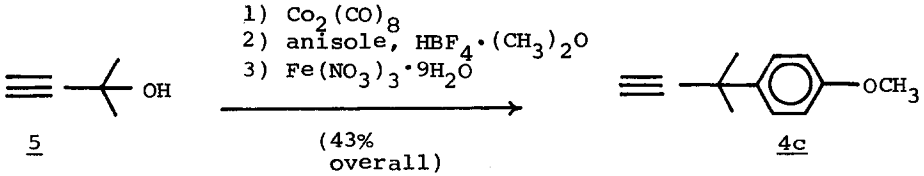
Table I. Alkylation of Anisole with $[HC{\equiv}CC(OH)R_1R_2]Co_2(CO)_6$ (2).

$[HC{\equiv}CC(OH)R_1R_2]Co_2(CO)_6$	Acid	3(%)	4(%)
2a ($R_1=R_2=H$)	TFA/TFAA[a]	31	46
2a	$HBF_4 \cdot Me_2O$[b]	35	49
2b ($R_1=Me, R_2=H$)	$HBF_4 \cdot Me_2O$[b]	25	53
2c ($R_1=R_2=Me$)	$HBF_4 \cdot Me_2O$[b]	--	78

[a] 0.1 equiv. TFA, 1.0 equiv. TFAA

[b] 2.0 equiv. $HBF_4 \cdot Me_2O$

Modifications in the alkylation procedure have been made which permit its extension to a wider range of substrates. Firstly, the reactions may be carried out in CH_2Cl_2 solution (0°) employing only a slight excess of the substrate with little decrease in yield. In this manner, phenol was alkylated with 2c in 72% yield. Secondly, it is possible to carry out the three step complexation-alkylation-decomplexation sequence in moderate overall yield without purification of intermediates. The following procedure for the conversion 5 → 4c is representative.



Solid $Co_2(CO)_8$ (3.45 g, 10.0 mmol) was added to a stirred solution of 5 (10.0 mmol) in 25 ml. of petroleum ether under N_2. After 2 hrs the solvent was removed under reduced pressure, replaced by 20 ml of CH_2Cl_2, and the resulting solution was added dropwise to a cooled (0°) CH_2Cl_2 solution containing 2.0 ml (18.5 mmol) of anisole and 2.5 ml (14.0 mmol) of $HBF_4{\cdot}Me_2O$. After standing overnight at 0°, the solution was treated with solid $NaHCO_3$, filtered, and the resulting filtrate concentrated at 25 mm. The residue was then dissolved in 20 ml of ethanol and treated with an excess of $Fe(NO_3)_3{\cdot}9H_2O$ until CO evolution ceased. Following a standard aqueous workup, evaporation of the combined ether extracts gave an orange liquid which was distilled at reduced pressure (0.2 mm). After a forerun of anisole (0.73 g), the product 4c (0.75 g, 43% based on 5) was obtained as a pale yellow liquid at 70-72°C.[7]

Several important features of this propargylation method are to be noted: 1) acid-catalyzed rearrangements, which plague uncomplexed propargylic alcohols,[8] are avoided; 2) quaternary centers may be generated α-to the synthetically versatile acetylene function[9] (e.g. $5 \rightarrow 4c$) and 3) since propargyl alcohols are derived from acetylide additions to carbonyl compounds, in effect, this method constitutes a flexible carbonyl geminal dialkylation, a process of considerable interest in natural product synthesis.[10]

Reactions of the cations 1 with other aromatic and non-aromatic nucleophilic substrates and applications of these reactions to the synthesis of selected natural products are underway.

Acknowledgments. We thank the Research Corporation and the Donors of the Petroleum Research Fund of the American Chemical Society for partial support. R.F.L. acknowledges a scholarship from the Brazilian government.

References and Notes

1) Reviews: M. Cais, Organometal. Chem. Rev., 1, 435 (1966); L. Haynes and R. Pettit in "Carbonium Ions", G.A. Olah and P.V.R. Schleyer, eds., vol. 5, Wiley, N.Y. (1975).

2) The only significant example is due to Ugi and coworkers (I. Ugi, Rec. Chem. Prog., 80, 289 (1969)) who have taken advantage of the retentive nucleophilic displacement of chiral α-ferrocenyl amines in effecting asymmetric four-component peptide synthesis.

3) R.E. Connor and K.M. Nicholas, J. Organometal. Chem., 125, C45 (1977); K.M. Nicholas and R. Pettit, ibid, 44, C21 (1972).

4) H.W. Sternberg, H. Greenfield, R.H. Friedel, J. Wotiz, R. Markby and I. Wender, J. Am. Chem. Soc., 76, 1457 (1956); R.S. Dickson and P.J. Fraser, Adv. in Organometal. Chem., 12, 323 (1974).

5) a) K.M. Nicholas and R. Pettit, Tetrahedron Lett., 37, 3475 (1971);
b) D. Seyferth and A. Wehman, J. Am. Chem. Soc., 92 5520 (1970).

6) Reaction complete $<$ 1 hr. for 1a, 1b, 2a, 2b; $<$ 18 hr. for 2c.

7) NMR (CS_2): δ 7.40(2H,d,J=8Hz), 6.8(2H,d,J=8Hz), 3.7(3H,s), 2.2(1H,s), 1.5(6H,s). MS : m/e=174(P).

8) J.H. Wotiz in "Chemistry of Acetylenes", E. Viehe (ed.), Marcel Dekker, N.Y., pp. 365-424 (1969).

9) An alternative approach to this problem involving the coupling of alkynylaluminums and 3° halides has recently been reported: E. Negishi and S. Baba, J. Am. Chem. Soc., 97, 7385 (1975).

10) B.M. Trost, D.E. Keeley, H.C. Arndt, J.H. Rigby and M.J. Bogdanowicz, J. Am. Chem. Soc., 99, 3080 (1977); B.M. Trost, M.J. Bogdanowicz, and A.J. Kern, ibid, 97, 2218 (1975); E.J. Corey and J.I. Schulman, ibid, 92, 5522 (1970).