A. Benzophenone. This ketone (1.27 g, 0.007 mol) gave a yellow solid which was recrystallized from aqueous ethanol to afford 1.4 g (61%) of 1,1-diphenyl-2-(3-quinolyl)ethanol (III): mp 178–180°; NMR (CDCl$_3$) δ 3.09–3.25 (s, 1, OH), 3.7 (s, 2, CH$_2$), 7.1–7.68 (m, 14, ArH), 7.75–8.35 (m, 2, ArH); ir (Nujol) 3200 cm^{-1} (OH).

Anal. Calcd for C$_{23}$H$_{19}$NO: C, 84.89; H, 5.89. Found: C, 85.00; H, 6.07.

B. 4,4'-Dimethylaminobenzophenone. The use of 2.5 g (0.007 mol) of this ketone gave a white solid which was recrystallized from benzene to yield 2.0 g (57%) of 1,1-bis[4-(dimethylamino)phenyl]-2-(3-quinolyl)ethanol (IV): mp 196–197° dec; NMR (CDCl$_3$) δ 2.95 (s, 12, CH$_3$), 3.72 (s, 2, CH$_2$), 6.6–6.92 (m, 4, ArH), 7.2–7.73 (m, 9, ArH), 8.38 (m, 1, ArH); ir (Nujol) 3175 cm^{-1} (OH).

Anal. Calcd for C$_{27}$H$_{29}$N$_3$O: C, 78.80; H, 7.10. Found: C, 79.07; H, 7.15.

C. p-Chlorobenzophenone. This ketone (1.5 g, 0.007 mol) gave a yellow solid which was recrystallized from aqueous ethanol to yield 0.8 g (32%) of 1-(4-chlorophenyl)-1-phenyl-2-(3-quinolyl)ethanol (V): mp 192.5–193.5°; NMR (CDCl$_3$) δ 3.5 (s, 1, OH), 3.75 (s, 2, CH$_2$), 7.1–7.84 (m, 13, ArH), 7.9–8.38 (m, 2, ArH); ir (Nujol) 3100 cm^{-1} (OH).

Anal. Calcd for C$_{23}$H$_{18}$ClNO: C, 76.75; H, 5.04. Found: C, 76.64; H, 5.12.

D. p-Chlorobenzaldehyde. This aldehyde (0.98 g, 0.007 mol) afforded a yellow gum which was recrystallized from methanol to give 0.7 g (34%) of 1-(4-chlorophenyl)-2-(3-quinolyl)ethanol (VI): mp 170–171.5°; NMR (TFA) δ 3.09–3.34 (d, 2, CH$_2$), 4.85–5.09 (t, 1, CH), 6.93 (s, 4, ArH), 7.59–7.94 (m, 4, ArH), 8.35–8.7 (s, 2, ArH); ir (Nujol) 3215 cm^{-1} (OH).

E. Chalcone. This ketone (1.5 g, 0.007 mol) gave a yellow gum that was recrystallized from benzene–petroleum ether (bp 30–60°) to afford 0.3 g (12%) of 1,3-diphenyl-3-hydroxy-3-(3-quinolylmethyl)-1-propene (VII): mp 215–216°; NMR (Me$_2$SO) δ 6.9–7.55 (m, ArH); ir (Nujol) 3500 (OH), 1660 (C=C), 965 cm^{-1} (C=CH).

Anal. Calcd for C$_{25}$H$_{21}$NO: C, 85.44; H, 6.02. Found: C, 85.62; H, 6.21.

F. Ethyl Bromide. This alkyl halide (0.76 g, 0.007 mol) gave 0.5 g (42%) of 3-n-propylquinoline (VIII): bp 138–141° (11 mm) [lit.[2] bp 137–140° (11 mm)]; n^{25}D 1.5921; picrate mp 173–174° (lit.[2] picrate mp 174–175°).

Registry No.—I, 612-58-8; II, 57443-81-9; III, 57443-82-0; IV, 57443-83-1; V, 57443-84-2; VI, 57443-85-3; VII, 57443-86-4; VIII, 20668-43-3; VIII picrate, 57443-87-5; LDIPA, 4111-54-0; benzophenone, 119-61-9; 4,4'-dimethylaminobenzophenone, 90-94-8; p-chlorobenzophenone, 134-85-0; p-chlorobenzaldehyde, 104-88-1; chalcone, 94-41-7; ethyl bromide, 74-96-4.

References and Notes

(1) (a) K. Ziegler and H. Zeiser, *Justus Liebigs Ann. Chem.*, **485**, 174 (1931); (b) F. W. Bergstrom, *J. Am. Chem. Soc.*, **53**, 3027 (1931); (c) F. W. Bergstrom and A. Moffat, *ibid.*, **59**, 1494 (1937); (d) M. J. Weiss and C. R. Hauser, *ibid.*, **71**, 2026 (1949); (e) for a more recent reference, see E. M. Kaiser and W. R. Thomas, *J. Org. Chem.*, **39**, 2659 (1974).
(2) R. W. Brown and G. Dougherty, *J. Am. Chem. Soc.*, **69**, 2232 (1947).
(3) W. P. Utermohlen, Jr., *J. Org. Chem.*, **8**, 544 (1943).

Organometallic Chemistry. VIII.[1] Protonated Anisolechromium Tricarbonyl and Its Carbon-13 Nuclear Magnetic Resonance Spectroscopic Study

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Arenechromium tricarbonyls undergo hydrogen–deuterium exchange in acid media, and it has been proposed that protonated species are intermediates in the reaction.[3] Protonated arenechromium tricarbonyls were first reported by Davison, McFarland, Pratt, and Wilkinson in 1962.[4] The hydrido hydrogen signals were observed at δ −3.5 to −4.0

1   2
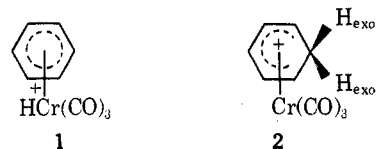
as singlets. Both metal-protonated 1 and ring-protonated 2 structures have been proposed. Based on the width of the hydride hydrogen absorption in comparison with the estimated $J_{exo,endo}$ coupling constants, a recent ^{1}H NMR study indicated that ring-protonated ion 2 cannot be the major species observed in solution.[5] Chromium protonated structure 1 is also indicated in protonated arenechromium triphenylphosphinedicarbonyls by the splitting of the signal corresponding to the hydrido hydrogen into a doublet due to a coupling with the ^{31}P nucleus.[6] We now report the preparation and carbon-13 NMR study of protonated anisolechromium tricarbonyl. We selected the methoxy substituent to enhance the ring π-donor ability of the system. Data obtained indicate that despite the powerful ring activating substituent the observed long-lived species contains the proton attached exclusively to the metal atom.

Results and Discussion

Anisolechromium tricarbonyl was protonated with FSO$_3$H in liquid SO$_2$ at −80° under nitrogen. The carbon-13 NMR spectral data of the protonated species as well of related model compounds are summarized in Table I.

Carbon-13 NMR spectroscopy seems to be a most suitable method for determining the structure of protonated arenechromium tricarbonyls. If protonation occurs on the aromatic ring, the ring carbons should exhibit characteristic shifts similar to areniumiron tricarbonyl cations.[7] The methylene carbon would show pronounced shielding in accordance with the transformation from aromatic sp^2 to aliphatic sp^3 hybridation upon protonation. Furthermore, the methylene carbon should appear as a triplet with J_{C-H} coupling corresponding to the sp^3 hybridization of the carbon. Based on the spectrum shown in Figure 1, the structure of protonated anisolechromium tricarbonyl is not consistent with formation of an arenium ion. If an arenium ion is formed, the C$_2$ and C$_6$ carbons should become most deshielded as in the case of the C$_6$H$_7$Fe(CO)$_3$ cation (Table I). The chemical shifts of all ring carbons are deshielded by about 8–17 ppm upon protonation, and the pattern of chemical shifts resemble that of the anisolemercurinium ion^{14} (Table I), where the aromatic ring is complexed with electron-deficient metal. There is no chemical shift observed corresponding to an aliphatic methylene carbon which would result at the site of protonation due to a change from sp^2 to sp^3 hybridization. There is also no triplet absorption corresponding to a methylene carbon or doublet of doublets corresponding to proton exchange involving ring proton. The increase of J_{C-H} coupling constants of all ring carbons also rules out ring protonation.

The structure of arenechromium tricarbonyls is of considerable interest. Benzenechromium tricarbonyl shows structure 3 with the Cr–CO bonds directed toward the midpoints of the C–C bonds of the ring.[8] Monosubstituted derivatives adopt either an eclipsed configuration 4 or a staggered configuration 5.[9] The temperature dependence of
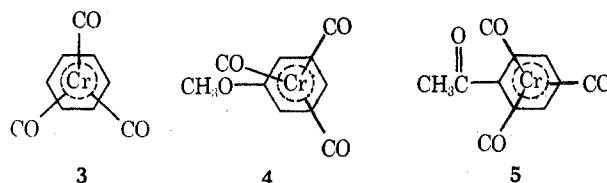

3   4   5

Table I
Carbon-13 NMR Parameters of Protonated Anisolechromium Tricarbonyl and Related Model Compounds[a]

Compd	C_1	C_2, C_6	C_3,C_5	C_4	OCH_3	CO	Ref
OCH₃ (anisole)	159.47 (s)	113.57 (d, 159)	128.95 (d, 159)	120.22 (d, 162)	55.36 (q, 143)		c
OCH₃ –Cr(CO)₃	143.68 (s)	78.68 (d, 173)	95.71 (d, 177)	85.95 (d, 177)	55.67 (q, 145)	233.53 (s)	c
OCH₃⁺ –Cr(CO)₃	151.24 (s)	95.69 (d, 183.4)	110.17 (d, 185.7)	100.12 (d, 184.4)	60.86 (q, 152.0)	224.26 (1)[b] (s) 220.42 (2) (s)	b
OCH₃ –Hg²⁺	192.6	118.4	139.0	105.2	57.0		d
–Fe(CO)₃ H H	99.43 (d, 179)	102.6 (d, 171)	92.58 (d, 162)	31.09 (t, 132)		208.12 (1)[b] (s) 198.36 (2) (s)	e
OCH₃ H H	192.9 (s)	122.3 (d) 128.5 (d)	168.7 (d) 175.5 (d)	41.9 (t)	54.4 (q)		f

[a] The spectra were obtained on a Varian XL-100 spectrometer. Chemical shifts in δ_{13C} (parts per million) are referred to the external capillary. Coupling constants in hertz and the multiplicities are given in parentheses: s = singlet; d = doublet; t = triplet; q = quartet. [b] In a ratio 1:2. [c] G. Bodner and L. J. Todd, *Inorg. Chem.*, 13, 361 (1974). [d] Reference 14. [e] Reference 7a. [f] G. A. Olah and Y. K. Mo, *J. Org. Chem.*, 38 353 (1973).
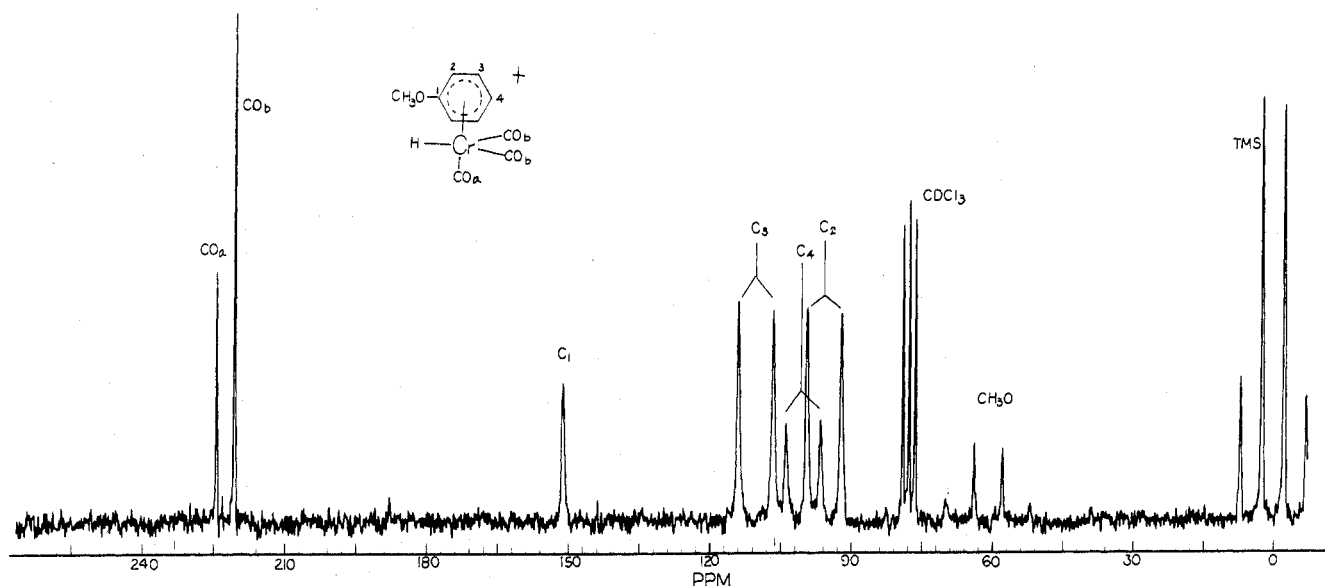

Figure 1. Proton coupled ^{13}C NMR spectrum of protonated anisolechromium tricarbonyl in SO_2 at $-70°$. (The structure shown is only one of the possible geometrical arrangements.)

the ^1H NMR spectra of arenechromium tricarbonyls has been proposed to be due to conformational equilibria indicating their fluxional nature in solution.[10,11] The rotation of the $Cr(CO)_3$ group relative to the arene ring is considered to be fast on the NMR time scale at all times. On the other hand, the resolution of two carbonyl resonances has been reported for cycloheptatriene–$Cr(CO)_3$ at $-60°$ [12] and for norbornadiene–$Cr(CO)_4$ at room temperature.[13] The present observation of two separate carbonyl resonances in protonated anisolechromium tricarbonyl with a ratio 1:2 indicates a slow exchange process at $-70°$ and at least Cs symmetry of the structure (as a consequence of either a conformational arrangement relating to the methoxy group or the arrangement of the carbonyls in the equatorial and

axial positions). The deshielding of ring carbons of anisolechromium tricarbonyl upon protonation can also be attributed to the increase of σ forward donation in bonding. The electron density is transmitted to the metal atom via σ forward donation and counterbalances the positive charge on the metal atom. The pertinent increase in shielding of the carbonyl resonances upon protonation is also consistent with the increase of the positive charge on the metal atom and the extent of metal–carbonyl σ forward donation.[15] However, we cannot rule out other factors which might contribute to the change of chemical shifts upon protonation.[16]

Observation of exclusively metal protonated anisolechromium tricarbonyl in FSO_3H–SO_2 solution at $-80°$, under

so-called long-lived, stable ion conditions, does not necessarily exclude the possibility that in the kinetically controlled initial protonation of anisolechromium tricarbonyl ring (or carbonyl) protonation may compete with metal protonation. The former, however, then would rapidly reverse, whereas the latter would not. Under stable conditions generally the thermodynamically most stable forms are observed, if the energy barrier of interconversion is sufficiently low at the studied temperature.

Experimental Section

Anisolechromium tricarbonyl (Strem Chemical, Inc.) was used without further purification. Protonation was carried out by adding a cold $DCCl_3$ solution of anisolechromium tricarbonyl into excess FSO_3H–SO_2 at −80° under nitrogen, to obtain an about 10% solution of protonated anisolechromium tricarbonyl in FSO_3H–SO_2. Both solutions were purged with nitrogen before mixing. FT carbon-13 spectra were obtained on Varian XL-100 NMR spectrometer using external Me_4Si capillary as reference, under experimental details described previously.

Registry No.—Protonated anisolechromium tricarbonyl, 57444-58-3.

References and Notes

(1) Part VII: G. A. Olah and S. H. Yu, *J. Org. Chem.,* **40**, 3638 (1975).
(2) Postdoctoral Fellow, 1973–1974.
(3) (a) D. N. Kursanov, V. N. Setkina, N. K. Baranetskaya,V. I. Zdanovich, and K. N. Anisimov, *Dokl. Akad. Nauk SSSR,* **190**, 1103 (1970); (b) V. N. Setkina, V. I. Zdanovich, N. K. Baranetskaya, A. I. Jurtanov, K. N. Anisimov, and D. N. Kursanov, *Zh. Obshch. Khim,* **41**, 1338 (1971).
(4) A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.,* 3653 (1962).
(5) C. P. Lillya and R. A. Sahatjian, *Inorg. Chem.,* **11**, 889 (1972).
(6) D. N. Kursanov, V. N. Setkina, P. V. Petrovskii, V. I. Zdanovich, and N. K. Baranetskaya, *J. Organomet. Chem.,* **37**, 339 (1972).
(7) (a) G. A. Olah, S. H. Yu, and G. Liang, submitted; (b) A. I. Rezvukhim, V. N. Plottukh-Peletskii, R. N. Berezina, and V. G. Shubin, *Izv. Akad. Nauk SSSR, Ser. Khim.,* 705 (1973).
(8) B. Rees and P. Coppens, *J. Organomet. Chem.,* **42**, C102 (1972).
(9) D. L. Carter, A. T. McPhail, and G. A. Sim, *J. Chem. Soc. A,* 1866 (1968); 1619, 228 (1967).
(10) (a) W. R. Jackson, W. B. Tennings, and R. Spratt, *Chem. Commun.,* 593 (1970); (b) W. R. Jackson, W. B. Tennings, S. C. Rennison, and R. Spratt, *J. Chem. Soc. B,* 1214 (1969); (c) D. E. F. Gracey, W. R. Jackson, W. B. Tennings, and S. C. Rennison, *Chem. Commun.,* 231 (1966).
(11) (a) G. Barbieri and T. Tadder, *Chem. Commun.,* 312 (1970); (b) J. T. Price and T. S. Sorenson, *Can. J. Chem.,* **46**, 516 (1968).
(12) C. G. Kreiter and M. Lang, *J. Organomet. Chem.,* **55**, C27 (1973).
(13) B. E. Mann, *J. Chem. Soc., Dalton Trans.,* 2012 (1973).
(14) G. A. Olah and S. H. Yu, manuscript in preparation.
(15) (a) G. Bodner and L. J. Tood, *Inorg. Chem.,* **13**, 1335 (1974); (b) O. A. Gansow, D. A. Schenayder, and B. Y. Kimura, *J. Am. Chem. Soc.,* **94**, 3406 (1972).
(16) J. Evans and J. R. Norton, *Inorg. Chem.,* **13**, 3042 (1974).

Carbon–Carbon Bond Formation via Organometallic Electrochemistry

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The use of electrochemistry for organic and organometallic synthesis is well documented in the literature. However, fewer studies have been conducted in which a deliberate attempt has been exerted to exploit organometallic electrochemistry for organic synthesis or more specifically for the formation of carbon–carbon bonds.[2] Further, published results suggest that transition metals in the lower valent states are probably responsible for promotion and/or catalysis of several organic reactions.[3] As a result of these

two ideas, we have embarked on an investigation of the formation of carbon–carbon bonds from the electrochemical reduction of readily available transition metal complexes in the presence of organic substrates. In this paper we wish to report our preliminary results and emphasize the macroscale synthetic utility of this technique for organic chemistry.

Although there are several stable low-valent transition metal complexes such as the metal carbonyls, π-allylnickel,[4] and bis(cyclooctadienyl)nickel[5] which are isolable and have been used for organic synthesis, they have some disadvantages. For example, they are often sensitive to air, may require reasonably sophisticated techniques to incorporate them into reaction mixtures, and may be useful only in stoichiometric amounts owing to catalyst inactivation through reaction. This reported work emphasizes an approach which generates active but nonisolable catalysts and offers some advantages over the previously mentioned complexes. For example, the acetylacetonate complexes of many transition metals are soluble in organic solvents, easily prepared,[6] have reasonable air and thermal stability, and are convenient to incorporate into a reaction medium. Another potential advantage offered by the electrochemical system for generating chemically active metal complexes is the continuous recycling of the catalyst in the event it is inactivated by oxidation. Thus, the need for stoichiometric quantities of metal complex may be alleviated. One of the limitations of this technique is that one must choose the proper metal and substrate such that the reduction potentials allow for electrochemical reduction of the desired chemical components.

Description of Electrochemical Cell and Reaction Components. Several organic halides are presently under investigation, but this article shall deal only with aliphatic, benzylic, and aromatic halides. Data resulting from these substrates are shown in Tables I, II, and III.

Nickel and iron acetylacetonate were chosen as the starting metal complex because (a) they both have reported reduction potentials below the potentials of the substrate halides; and (b) they have isolable (Ni) and nonisolable (Fe) low-valent metal complexes which could be helpful later in the detailed investigations. There have only been a few σ-bonded aliphatic iron complexes isolated.[7] Since the metal complexes are being reduced to lower oxidation states, substances such as triphenylphosphine (Ph_3P), which are referred to in this paper as stabilizing ligands, were added to (a) modify the activity and (b) perhaps aid in the solubility of the reduced metal. In reactions run without Ph_3P, the solution becomes cloudy and the cathode develops a coating. However, neither of these two conditions appeared to adversely affect the product yields or distribution (Table II).

A diagram of the electrochemical cell used in this study is shown in Figure 1. Electrodes were made from sheet metal (Al, Cu, or Ni) which was cut to the dimensions of 45 × 45 × 0.90 mm and cleaned thoroughly just prior to use. In the cell these plates were placed parallel to one another with a 6–8-mm space between them. A potential was applied across the electrodes by a constant voltage power supply, which was automaatically regulated such that the potential on the cathode relative to SCE was more cathodic than the reduction potential of the metal complex [Fe(acac)$_3$[2] −0.82 V vs. SCE in THF; Ni(acac)$_2$[2] −1.5 V vs. SCE in DMF] and less cathodic than the reported substrate reduction potentials (aliphatic bromides[8] −2.2 V vs. SCE in DMF; bromobenzene[8] −2.3 V vs. SCE in DMF; benzyl bromide[8,9] −1.22 V vs. SCE in DMF). The standard calomel electrode was periodically inserted directly behind the cathode during the reaction to obtain an approximate