as solids or as solutions in dry CH_3CN. Representative reactions are detailed below.

Preparation of VBr_2(salen). To a well-stirred, colorless solution of Ph_3PBr_2 (prepared by reaction of 2.63 g (0.01 mol) of Ph_3P with 0.51 mL (0.01 mol) of Br_2) in 150 mL of dry CH_3CN was added 3.33 g (0.01 mol) of powdered green VO(salen) over a 30-min period under N_2. The resulting black mixture was stirred for 24 h, and the solid product was filtered under N_2, washed with cold dry CH_3CN, dried overnight in vacuo, and stored in the drybox. The yield was 3.97 g (87%). Anal. Calcd for $VBr_2N_2C_{16}H_{14}$: V, 10.68; Br, 33.50; N, 5.87; C, 40.28; H, 2.96. Found: V, 8.48; Br, 33.25; N, 6.22; C, 40.57; H, 3.34.

Reaction of $VO(acac)_2$ with Ph_3PBr_2. Over a 20-min period a solution of 2.65 g (0.01 mol) of $VO(acac)_2$ in 500 mL of CH_3CN was added to a solution of 0.02 mol of Ph_3PBr_2 in 75 mL of CH_3CN, prepared as described above. As the addition proceeded, the solution changed color from water-white to yellow, gold, amber, and dark olive-brown. The resulting solution was vacuum evaporated to a volume of 20 mL and extracted with 150 mL of dry benzene. The light blue solid which precipitated was filtered and recrystallized from 50:50 benzene–chloroform. The yield was 6.5 g (83%). Anal. Calcd for $VBr_2C_{36}H_{30}P_2O_3$: V, 6.50; Br, 20.40; C, 55.20; H, 3.86; P, 7.91. Found: V, 6.11; Br, 19.74; C, 54.38; H, 3.65; P, 7.53.

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Registry No. V=O(salen), 36913-44-7; V=S(salen), 74354-69-1; V=O(acen), 19195-97-2; V=S(acen), 74354-70-4; VBr_2(salen), 74498-60-5; VCl_2(salen), 70629-75-3; $V{=}OBr_2(O{=}PPh_3)_2$, 74498-61-6; $V{=}OCl_2(O{=}PPh_3)_2$, 16997-35-6; B_2S_3, 12007-33-9; Ph_3PBr_2, 1034-39-5; $VO(acac)_2$, 3153-26-2.

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Synthesis of Ring-Substituted Derivatives of Cyclopentadienyl Tricarbonyl Complexes of Molybdenum and Tungsten

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The ions $(C_5H_4R)^-$ (R = COMe or CO_2Me), generated by electroreduction of $Fe(\eta^5\text{-}C_5H_4R)_2$ in DMF or THF, react with $M(CO)_3L_3$ (M = Mo or W, L = THF or DMF), giving $[M(\eta^5\text{-}C_5H_4R)(CO)_3]^-$. Treatment of these carbonylate ions with MeI affords $M(\eta^5\text{-}C_5H_4R)(CO)_3CH_3$, and their electrooxidation gives either $[M(\eta^5\text{-}C_5H_4R)(CO)_3]_2$ or $[M(\eta^5\text{-}C_5H_4R)(CO)_3]_2Hg$ depending on the working electrode employed. Oxidation of $[M(\eta^5\text{-}C_5H_4R)(CO)_3]_2$ with iodine produces $M(\eta^5\text{-}C_5H_4R)(CO)_3I$. The new complexes have been characterized by spectroscopic and electroanalytical methods, and it is suggested that the bulky nature of the R substituent inhibits free rotation about the ring–metal bond.

Introduction

There are, at present, no reports of electrophilic or nucleophilic attack on the cyclopentadienyl rings in $[M(\eta^5\text{-}C_5H_5)(CO)_3]_2$. That this is so is due almost certainly to the oxidative and reductive instability of these dimers. Thus under oxidizing conditions, $[M(\eta^5\text{-}C_5H_5)(CO)_3]_2$ and also $M(\eta^5\text{-}C_5H_5)(CO)_3Q$ (Q = alkyl, aryl, or halide) decompose and so, for example, Friedel–Crafts alkylation or acylation reactions are impossible. In reducing media the dimers readily form the stable carbonylate ions $[M(\eta^5\text{-}C_5H_5)(CO_3]^-$ which easily undergo addition reactions, but at the metal and not the ring.[1,2]

The synthesis of chromium, molybdenum, or tungsten tricarbonyl complexes containing substituted cyclopentadienyl rings can be achieved by four methods: the reaction of $M(CO)_6$ with appropriately substituted cyclopentadienide anions,[3–7] substituted cyclopentadienes,[8,9] or fulvenes[10,11] or treatment of $M(\eta^5\text{-}C_5H_4R)_2H_2$ with CO and BF_3 under pressure in the presence of an aliphatic alcohol.[12] Somewhat exceptionally, $[Mo(\eta^5\text{-}C_5H_4Et)(CO)_3]_2$ can be prepared in very low yield[13] by thermolysis of $Mo(\eta^5\text{-}C_5H_5)(CO)_3Et$. All of the complexes prepared in these ways contain alkyl-ring substituents and, to our knowledge, no compounds containing electron-withdrawing substituents (e.g., COR or CO_2R) have been described.

In our study of the electrochemical reduction of ferrocene derivatives, we showed[14] that $Fe(\eta^5\text{-}C_5H_4R)_2$ is readily decomposed, following a two-electron transfer, to cyclopentadienide ions and metallic iron. Of particular interest in this reaction is the easy formation of substituted cyclopentadienide anions from readily accessible ferrocenyl derivatives. Thus, the ions $(C_5H_4COMe)^-$ or $(C_5H_4CO_2Me)^-$, which are very difficult or even impossible to prepare by conventional methods, are easily obtained, and we have described their use in the syntheses of new metallocene derivatives of cobalt and rhodium.[14]

It was of importance to us to see whether this convenient synthetic route could be extended to the preparation of tricarbonyl compounds of Mo- and W-containing cyclopentadienyl rings substituted by electron-withdrawing groups. Our study was restricted to compounds of Mo and W because

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(1) G. E. Coates, M. L. H. Green, and K. Wade, "Organometallic Compounds", Vol. II, Chapman and Hall, London, 1972, p 118.
(2) R. B. King, "Advances in Organometallic Chemistry", Vol. 2, F. G. A. Stone and R. West, Eds., Academic Press, New York, 1964, p 190.
(3) B. Nicholls and M. C. Whiting, *J. Chem. Soc.*, 551 (1959).
(4) E. O. Fisher, K. Ofele, H. Essler, W. Fröhlich, J. P. Mortenson, and W. Semmlinger, *Chem. Ber.*, **91**, 2763 (1958).
(5) G. Natta, R. Ercoli, and F. Calderazzo, *Chim. Ind.* (*Milan*), **40**, 287 (1958).
(6) E. O. Fisher, W. Hafner, and H. O. Stahl, *Z. Anorg. Allg. Chem.*, **282**, 47 (1955).
(7) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956).
(8) L. T. Reynolds and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **9**, 86 (1959).
(9) R. B. King and A. Efraty, *J. Am. Chem. Soc.*, **93**, 4950 (1971).
(10) R. B. King and M. B. Bisnette, *Inorg. Chem.*, **3**, 801 (1964).
(11) E. W. Abel, A. Singh, and G. Wilkinson, *J. Chem. Soc.*, 1321 (1960).
(12) J. Koziokowski, V. Norman, and T. P. Whaley, U.S. Patent 3 253 946 (1966).
(13) "Gmelins Handbook der anorganischen Chemie", Vol. 3, Verlag Chemie, Weinheim/Bergstr., Germany, 1971, p 160.
(14) N. El Murr, A. Chaloyard, and E. Laviron, *Nouv. J. Chim.*, **2**, 15 (1978).

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Table I

	voltammetry,[a] V (on carbon)	IR, cm^{-1}	NMR, ppm ($CDCl_3$)	yields,[g] %	mp, °C
$[(CH_3COC_5H_4)W(CO)_3]^-$	+0.20[b]	1895, 1780 (br), 1670			
$(CH_3COC_5H_4)W(CH_3)(CO)_3$	−1.76[c]	2027, 1946, 1938, 1705[e]	5.95 (t, 2), 5.80 (t, 2), 2.35 (s, 3), 0.05 (s, 3)	63	73
$[(CH_3COC_5H_4)W(CO)_3]_2$	−0.80[c]	1969, 1919, 1695[d]		65	210
$(CH_3COC_5H_4)W(I)(CO)_3$	−0.83[c]	2060, 1982, 1685	6.00 (t, 2), 5.75 (t, 2), 2.40 (s, 3)	50	96
$[(CH_3CO_2C_5H_4)W(CO)_3]^-$	+0.16[b]	1901, 1790 (br), 1722			
$(CH_3CO_2C_5H_4)W(CH_3)(CO)_3$	−1.82[c]	2027, 1942, 1746[e]	5.95 (t, 2), 5.75 (t, 2), 3.80 (s, 3), 0.05 (s, 3)	75	74
$[(CH_3CO_2C_5H_4)W(CO)_3]_2$	−0.95[c]	1970, 1915, 1722[f]		55	201
$(CH_3CO_2C_5H_4)W(I)(CO)_3$	−0.88[c]	2059, 1975, 1715[e]	6.05 (t, 2), 5.80 (t, 2), 2.35 (s, 3)	40	109
$[(CH_3COC_5H_4)Mo(CO)_3]^-$	+0.22[b]	1900, 1800 (br), 1670[d]			
$(CH_3COC_5H_4)Mo(CH_3)(CO)_3$	−1.62[c]	1955, 1947, 2030, 1704[e]	6.00 (t, 2), 5.80 (t, 2), 2.40 (s, 3), 0.05 (s, 3)	61	66
$[(CH_3COC_5H_4)Mo(CO)_3]_2$	−0.83[c]	1970, 1918, 1680[f]		60	197
$(CH_3COC_5H_4)Mo(I)(CO)_3$	−0.82[c]	2059, 1984, 1695[f]	5.95 (t, 2), 5.66 (t, 2), 2.35 (s, 2)	57	88
$[(CH_3CO_2C_5H_4)Mo(CO)_3]^-$	+0.22[b]	1912, 1800 (br), 1722			
$(CH_3CO_2C_5H_4)Mo(CH_3)(CO)_3$	−1.80[c]	2030, 1950, 1743[e]	5.85 (t, 2), 5.60 (t, 2), 3.75 (s, 3), 0.04 (s, 3)	62	77
$[(CH_3CO_2C_5H_4)Mo(CO)_3]_2$	−0.80[c]	1969, 1922, 1730[e]	5.99 (t, 2), 5.85 (t, 2), 3.60 (s, 3)	75	170
$(CH_3CO_2C_5H_4)Mo(I)(CO)_3$	−0.87[c]	2042, 1975, 1735[e]	6.05 (t, 2), 5.72 (t, 2), 3.85 (s, 3)	70	115

[a] Peak potentials; in THF; (n-Bu_4N)(PF_6) as supporting electrolyte. [b] Anodic potential vs. SCE. [c] Cathodic potential vs. SCE. [d] Spectrum taken in CH_2Cl_2. [e] Spectrum taken in hexane. [f] Spectrum taken in chloroform. [g] Yields are calculated in comparison with starting ferrocenes.

of the known lower stability of chromium analogues.[1,2]

Results and Discussion

Synthesis. The carbonylate ions $[M(\eta^5\text{-}C_5H_5)(CO)_3]^-$ can be obtained in good yield by reaction of $(C_5H_5)^-$ with $M(CO)_6$ (reaction 1). This reaction may be achieved in diglyme,

$$M(CO)_6 + (C_5H_5)^- \rightarrow [M(C_5H_5)(CO)_3]^- + 3CO \quad (1)$$

dioxane, tetrahydrofuran, 1,2-dimethoxyethane, or dimethylformamide[2] and requires refluxing conditions for several hours. The loss of CO seems to be easier from Mo than that from W, and it would appear that in coordinating solvents the reaction takes place in two stages (reaction 2).

$$M(CO)_6 + 3S \rightarrow M(CO)_3S_3 + 3CO$$

$$M(CO)_3S_3 + (C_5H_5)^- \rightarrow [M(C_5H_5)(CO)_3]^- + 3S \quad (2)$$

The electrolysis of ferrocene may be accomplished either in DMF or in THF, in the presence of (n-Bu_4N)(PF_6) as supporting electrolyte, as shown in reaction 3. Thus we have

$$Fe(C_5H_4R)_2 + 2e^- \xrightarrow[\text{DMF or THF}]{(Bu_4N)(PF_6)} 2(Bu_4N)(C_5H_4R) + Fe + 2PF_6^- \quad (3)$$

carried out the electrolysis of $Fe(\eta^5\text{-}C_5H_4R)_2$ (R = COMe or CO_2Me) in either THF or DMF and after removal of metallic iron have added the substituted cyclopentadienide anion to a solution containing preformed $M(CO)_3L_3$ (L = THF or DMF, as appropriate). However, we observed that complete removal of THF from $W(CO)_3(THF)_3$ did not occur on addition of $(C_5H_4R)^-$ in THF, although efficient substitution occurred with the molybdenum analogue. In DMF, no retention of solvent at the metal was observed, but, despite this apparent advantage, we prefer to use THF as the reaction medium because of the relatively easier workup procedures. In order to obtain the tungsten complexes, we first prepared $W(CO)_3(DMF)_3$ and then dissolved it in THF and added the solution to $(C_5H_4R)^-$ in THF;[15] the yields of the tungsten complexes are then similar to those of their molybdenum analogues.

It proved impossible to isolate (n-Bu_4N)$[M(\eta^5\text{-}C_5H_4R)(CO)_3]$ because of the difficulty of separation from a large excess of (n-Bu_4N)(PF_6), but the metalate ions were subsequently used without further purification.

An interesting characteristic of $[M(\eta^5\text{-}C_5H_4R)(CO)_3]^-$ (M = Mo or W; R = CO_2Me or COMe) is their considerable stability in relation to water and to oxidizing agents. Thus, the solutions can be handled in air for limited periods, and under inert atmospheres THF solutions of the carbonyl metalates do not deteriorate over several months.

In THF, $[M(\eta^5\text{-}C_5H_4R)(CO)_3]^-$ reacts very rapidly with methyl iodide (reaction 4), giving the corresponding methyl

$$[M(C_5H_4R)(CO)_3]^- + CH_3I \xrightarrow{\text{THF}} M(C_5H_4R)(CO)_3 + I^- \quad (4)$$

complex in good yield with respect to the precursor ferrocenyl derivatives.

In contrast to the carbonyl metalate ions, the methyl complexes can be easily separated from the base electrolyte. Thus after evaporation of THF solution, they can be extracted from the residue by using ether, and crystallization from ether/hexane mixtures effects complete separation from (n-Bu_4N)(PF_6) and other impurities in the electrolyte mixture.

Oxidation of $[M(\eta^5\text{-}C_5H_4R)(CO)_3]^-$ readily affords the corresponding binuclear compounds and can be achieved by chemical reagents[16] or by electrochemical methods.[17] If oxidation is achieved electrolytically, then the nature of the product depends on the electrode used: over mercury, the oxidized product is $[M(\eta^5\text{-}C_5H_4R)(CO)_3]_2Hg$, but, at a Pt working electrode, $[M(\eta^5\text{-}C_5H_4R)(CO)_3]_2$ is formed cleanly. Since these dimers are very insoluble, they precipitate from the reaction medium and are collected by filtration.

Despite the relative insolubility of $[M(\eta^5\text{-}C_5H_4R)(CO)_3]_2$ in organic solvents, it is possible to investigate their electrochemical properties (in DMF) and also to obtain $M(\eta^5\text{-}C_5H_4R)(CO)_3I$ by their reaction in chloroform with iodine (reaction 5). The iodo derivatives are soluble in chloroform and can be recrystallized from chloroform/hexane mixtures.

$$[M(C_5H_4R)(CO)_3]_2 + I_2 \rightarrow 2M(C_5H_4R)(CO)_3I \quad (5)$$

Spectroscopic and Electrochemical Studies (See Table I). (a) The IR spectra of almost all the new complexes exhibit three strong absorptions in the range 1600–2100 cm^{-1}: two associated with M–CO stretching modes and the third with ν(CO) of the COMe or CO_2Me group. The M–CO stretching modes of the complexes where R = COMe or CO_2Me appear at slightly higher frequencies than the corresponding bands when R = H or alkyl, and this is presumably due to the

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(15) A. Salzer, *J. Organomet. Chem.*, **107**, 79 (1976).

(16) E. O. Fisher and H. P. Fritz, *Adv. Inorg. Chem. Radiochem.*, **1**, 108 (1959).

(17) R. E. Dessy, F. E. Stary, R. B. King, and M. Waldrop, *J. Am. Chem. Soc.*, **88** 471 (1966).

electron-withdrawing properties of the R substituent in the former group of complexes.

In contrast to these general observations, the IR spectrum of $M(C_5H_4COMe)(CO)_3CH_3$ exhibits three absorptions in the metal–carbonyl region. We believe that, since the compound is obviously pure, this effect can only be explained by invoking the presence of isomers caused by the bulky nature of the COMe group and its prevention of free rotation about the ring–metal bond.

(b) The NMR spectra of the soluble complexes exhibited two triplets associated with the cyclopentadienyl ring protons. This is consistent with an A_2B_2 system and is entirely analogous to the situation in $Fe(\eta^5\text{-}C_5H_4R)_2$. However, in comparison with the ferrocene derivatives, these signals in the carbonyl complexes resonate at lower fields, presumably because of the electron-withdrawing effect of the $M(CO)_3$ group. Of the metal–metal bonded dimers, only $[Mo(\eta^5\text{-}C_5H_4CO_2Me)(CO)_3]_2$ was sufficiently soluble to give a ^1H NMR spectrum.

(c) Mass spectral examination, via the chemical ionization technique, provided confirmatory evidence of the nature of the complexes we have prepared. In all cases, except for $[M(\eta^5\text{-}C_5H_4R)(CO)_3]_2$, the molecular ion Q^+, as well as ions corresponding to $[Q - CO]^+$, $[Q - 2CO]^+$, and $[Q - 3CO]^+$ could be detected; for the methyl and iodo complexes, ions corresponding to $[Q - 3CO - CH_3]^+$ and $[Q - 3CO - I]^+$ could also be detected. A study of the fragmentation of the dimeric species showed, in addition to ions corresponding to $[Q/2]^+$, $[Q/2 - CO]^+$, $[Q/2 - 2CO]^+$ and $[Q/2 - 3CO]^+$, a series of ions corresponding to $[Q - 2CO]^+$, $[Q - 4CO]^+$, and $[Q - 6CO]^+$. This latter observation may reflect the stability of the M–M bond in these dimers.

(d) The electrochemical behavior of $[M(\eta^5\text{-}C_5H_5)(CO)_3]_2$ has already been examined by Dessy and his collaborators.[17] The electrochemical reduction of these homobimetallic complexes is irreversible and required two electrons. The reduction effects the scission of the metal–metal bond and formation of the carbonyl metalate ions (reaction 6).

$$[M(C_5H_5R)(CO)_3]_2 + 2e^- \rightarrow 2[M(C_5H_4R)(CO)_3]^- \qquad (6)$$

A qualitative correlation between $E_{1/2}$ for this reduction process and the energy of the M–M bond has been made, and it appears that the half-wave potential becomes more cathodic as the bond strength increases. The nucleophilicity of the anions $[M(C_5H_4R)(CO)_3]^-$ (R = H) has been indicated by an examination of their oxidation potentials with respect to an inert electrode. Thus, as the potential becomes more cathodic, the nucleophilicity seems to increase. Using these electrochemical methods, Dessy et al.[18] have claimed that $[Mo(C_5H_5(CO)_3]^-$ is approximately 7 times less nucleophilic than its tungsten analogue, the difference between their oxidation potentials being ca. 0.45 V. In relation to the new species $[M(C_5H_4R)(CO)_3]^-$ prepared here (M = Mo or W; R = COMe or CO_2Me), we observe *no* differences in their oxidation potentials in relation either to the metal or to the substituent R. That the oxidation potentials of these anions are positive with respect to the reference electrode is a reflection of their stability.

The cyclic voltammetry of solutions of $[M(\eta^5\text{-}C_5H_4R)(CO)_3]^-$ (R = COMe or CO_2Me) at a glassy carbon or Pt electrode, reveals an irreversible one-electron process. After oxidation, a cathodic wave due to $[M(C_5H_4R)(CO)_3]_2$ can be observed, and this has been confirmed by controlled-potential electrolyses. With use of this method, of course, the dimers can readily be prepared from the carbonylate anions (reaction 7).

$$[M(C_5H_4R)(CO)_3]^- \xrightarrow{-1e^-} [M(C_5H_4R)(CO)_3]\cdot$$
$$2[M(C_5H_4R)(CO)_3]\cdot \rightarrow [M(C_5H_4R)(CO)_3]_2 \qquad (7)$$

The reduction potentials of these dimers are virtually identical and are similar to the values reported by Dessy et al.[19] for the species where R = H. Thus it would appear that the ring substituents have little or no influence on the metal–metal bond.

The species $M(\eta^5\text{-}C_5H_4R)(CO)_3CH_3$ is reduced at a Pt electrode in an irreversible one-electron step, leading to $[M(\eta^5\text{-}C_5H_4R)(CO)_3]^-$ (identified electrochemically) and, presumably, $CH_3\cdot$. The latter presumably dimerizes, giving C_2H_6, or abstracts H· from the solvent, giving CH_4. However, if the reduction is carried out with the use of a mercury electrode, the carbonylate anion is again formed, but a cathodic wave at −2.05 V is observed, which corresponds to the reduction of $Hg(CH_3)_2$.[20]

The compound $M(\eta^5\text{-}C_5H_4R)(CO)_3I$ is reduced in a two-electron-transfer process (reaction 8).

$$M(C_5H_4R)(CO)_3I + 2e^- \rightarrow [M(C_5H_4R)(CO)_3]^- + I^- \qquad (8)$$

Conclusion

The work described in this paper shows that cyclopentadienide ions carrying electron-withdrawing substituents can be relatively easily generated by the electroreduction of appropriately substituted and readily available ferrocenes. The cyclopentadienide ions so produced can then be used to form molybdenum or tungsten carbonylate ions, $[M(\eta^5\text{-}C_5H_4R)(CO)_3]^-$ (M = Mo or W; R = COMe or CO_2Me) by reaction with suitable carbonyl derivatives. The carbonylate ions so produced have chemical properties typical of this class of compound.[1] To our knowledge, this is the first time that cyclopentadienyl carbonyl complexes of Mo or W have been prepared where electron-withdrawing groups are attached to the ring.

Experimental Section

Cyclic voltammograms (scan rate 0.1 V s^{-1}) and polarograms were obtained with the use of an EPL2 Tacussel instrument using a saturated calomel reference electrode (SCE). IR and ^1H NMR spectra were measured by using Beckman IR-12 and JEOL 60HL spectrometers, respectively. Mass spectra were obtained with a Finnigan 3300 machine. All reactions were carried out under argon.

$(n\text{-}Bu_4N)(C_5H_4CO_2Me)$ in Solution. $Fe(C_5H_4CO_2Me)_2$ (1 g, 3.4 mmol) in THF (100 cm^3, dried on Na/benzophenone and redistilled) containing $(n\text{-}Bu_4N)(PF_6)$ (0.2 M) was electrolyzed on mercury. The solution so obtained was filtered to remove metallic Fe and stored under argon.

$(n\text{-}Bu_4N)[Mo(\eta^5\text{-}C_5H_4CO_2Me)(CO)_3]$ in Solution. To 50 cm^3 of the solution prepared as above was added $Mo(CO)_6$ (0.9 g). The mixture was refluxed under argon for 2 h and then stored under argon.

$(n\text{-}Bu_4N)[W(\eta^5\text{-}C_5H_4CO_2Me)(CO)_3]$ in Solution. To a solution (50 cm^3) of $(n\text{-}Bu_4N)(C_5H_4CO_2Me)$ in THF was added $W(CO)_3(DMF)_3$ (1.2 g). The mixture was refluxed for 3 h under argon and then stored.

$Mo(\eta^5\text{-}C_5H_4CO_2Me)(CO)_3CH_3$. To a solution (25 cm^3) of $(n\text{-}Bu_4N)[Mo(\eta^5\text{-}C_5H_4CO_2Me)(CO)_3]$ (prepared as described above) was added methyl iodide (1 cm^3), and the mixture was shaken for 30 min. THF was then evaporated and the residue extracted by using diethyl ether. The extract was evaporated to dryness, and the residue was recrystallized from an ether/hexane (1:1 v/v) mixture. The yield of the air-stable, yellow solid was 0.33 g.

$[Mo(\eta^5\text{-}C_5H_4CO_2Me)(CO)_3]_2$. A solution of $(n\text{-}Bu_4N)[Mo(\eta^5\text{-}C_5H_4CO_2Me)(CO)_3]$ (25 cm^3) was electrolyzed with use of a Pt electrode at +0.3 V. A blood red solution was formed which was evaporated to dryness. The residue was recrystallized from a hexane/chloroform mixture (ca. 1:4 mixture v/v) giving a red, air-stable solid (yield 0.38 g).

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(18) R. E. Dessy, R. L. Pohl, and R. B. King, *J. Am. Chem. Soc.*, **88**, 5121 (1966).

(19) R. E. Dessy, P. M. Weissman, and R. L. Pohl, *J. Am. Chem. Soc.*, **88**, 5117 (1966).

(20) G. A. Tedoradze, *J. Organomet. Chem.*, **88**, 1 (1975).

$\mathrm{Mo(\eta^5\text{-}C_5H_4CO_2Me)(CO)_3I}$. To a solution of $\mathrm{[Mo(\eta^5\text{-}C_5H_4CO_2Me)(CO)_3]_2}$ (0.2 g) in chloroform (40 $\mathrm{cm^3}$) in a Schlenk tube was added dropwise iodine (0.16 g) in chloroform (20 $\mathrm{cm^3}$). The mixture was shaken for 30 min and then washed with aqueous thiosulfate ion (three times) to remove iodine. The organic phase was then separated and dried and on evaporation afforded a solid. This was recrystallized from a hexane/chloroform mixture (1:1 v/v), affording orange-red flakes of the complex (yield 0.2 g).

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Registry No. $\mathrm{(\textit{n}\text{-}Bu_4N)(C_5H_4CO_2Me)}$, 74449-25-5; $\mathrm{(\textit{n}\text{-}Bu_4N)[Mo(\eta^5\text{-}C_5H_4CO_2Me)(CO)_3]}$, 74466-22-1; $\mathrm{(\textit{n}\text{-}Bu_4N)[W(\eta^5\text{-}C_5H_4CO_2Me)(CO)_3]}$, 74482-37-4; $\mathrm{Mo(\eta^5\text{-}C_5H_4CO_2Me)(CO)_3CH_3}$, 73249-51-1; $\mathrm{[Mo(\eta^5\text{-}C_5H_4CO_2Me)(CO)_3]_2}$, 74466-23-2; $\mathrm{Mo(\eta^5\text{-}C_5H_4CO_2Me)(CO)_3I}$, 74482-38-5; $\mathrm{[(CH_3COC_5H_4)W(CO)_3]^-}$, 74466-24-3; $\mathrm{(CH_3COC_5H_4)W(CH_3)(CO)_3}$, 73249-59-9; $\mathrm{[(CH_3COC_5H_4)W(CO)_3]_2}$, 74466-25-4; $\mathrm{(CH_3COC_5H_4)W(I)(CO)_3}$, 74466-26-5; $\mathrm{(CH_3CO_2C_5H_4)W(CH_3)(CO)_3}$, 73243-43-3; $\mathrm{[(CH_3CO_2C_5H_4)W(CO)_3]_2}$, 74466-27-6; $\mathrm{(CH_3CO_2C_5H_4)W(I)(CO)_3}$, 74466-28-7; $\mathrm{[(CH_3COC_5H_4)Mo(CO)_3]^-}$, 74466-29-8; $\mathrm{(CH_3COC_5H_4)Mo(CH_3)(CO)_3}$, 73243-46-6; $\mathrm{[(CH_3COC_5H_4)Mo(CO)_3]_2}$, 74482-39-6; $\mathrm{(CH_3COC_5H_4)Mo(I)(CO)_3}$, 74466-30-1; $\mathrm{Fe(C_5H_4CO_2Me)_2}$, 1273-95-6; $\mathrm{Mo(CO)_6}$, 13939-06-5; $\mathrm{W(CO)_3(DMF)_3}$, 59561-69-2; MeI, 74-88-4; $\mathrm{I_2}$, 7553-56-2.

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Preparation and Characterization of Platinum(II) Complexes Pt(P-C)LX, Where (P-C) Is Metalated Tri-*tert*-butylphosphine

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Reaction of tri-*tert*-butylphosphine with *trans*-$\mathrm{PtCl_2(NCPh)_2}$ in a 2:1 molar ratio in dichloromethane results in the formation of the chloro-bridged dimeric complex $\mathrm{[PtCl(\textit{t}\text{-}Bu_2PCMe_2CH_2)]_2}$ (**2**) along with *trans*-$\mathrm{PtCl(\textit{t}\text{-}Bu_2PCMe_2CH_2)(P\text{-}\textit{t}\text{-}Bu_3)}$ (**1**) and $\mathrm{(\textit{t}\text{-}Bu_3PH)Cl}$. Complex **2** is also prepared by displacing $\mathrm{\textit{t}\text{-}Bu_3P}$ from complex **1** by reaction with mercuric chloride in benzene. Reaction of complex **1** with $\mathrm{PtCl_2(NCPh)_2}$ also produces the dimeric complex **2**, when the reaction is carried out in refluxing benzene. Bridge-splitting reactions of **2** with various ligands give the complexes $\mathrm{PtCl(\textit{t}\text{-}Bu_2PCMe_2CH_2)(L)}$ (**5**) (where L = pyridine, CO, $\mathrm{Me_2S}$, $\mathrm{AsPh_3}$, $\mathrm{Ph_3Sb}$, $\mathrm{Ph_3P}$, $\mathrm{Et_3P}$, $\mathrm{Ph_2MeP}$, $\mathrm{\textit{i}\text{-}Pr_3P}$, $\mathrm{c\text{-}Hx_3P}$, $\mathrm{\textit{t}\text{-}Bu_2MeP}$, $\mathrm{\textit{t}\text{-}BuPh_2P}$, and $\mathrm{\textit{t}\text{-}Bu_3P}$) which have been characterized by elemental analyses as well as proton and ^{31}P NMR spectral studies. The trans configuration of complexes **5** containing two nonequivalent phosphine ligands is established by the large phosphorus–phosphorus couplings ($J(\mathrm{PP'})$) of the order of $\simeq$400 Hz.

Introduction

The intramolecular metalation which occurs between the metal and the C–H bonds of *tert*-alkyl- or arylphosphines in palladium or platinum complexes results in the formation of metal–carbon bonds.[1,2] The process is believed to be promoted by the facile formation of five-membered rings[3] and is also dependent on the steric bulkiness of the phosphine ligands. However, comparatively few examples[4–6] of the intramolecular metalation of the purely aliphatic phosphines are known compared with arylphosphines. Recently, we described intramolecular metalations of tri-*tert*-butylphosphine in platinum[7] and palladium[8] hydrides leading to the formation of $\mathrm{MX(P\text{-}C)(\textit{t}\text{-}Bu_3P)}$ (**1**) (M = Pd, Pt; P-C = $\mathrm{\textit{t}\text{-}Bu_2PCMe_2CH_2}$; X = Cl, Br, I, $\mathrm{CF_3CO_2}$). Compound **1** was also obtained from the reaction of $\mathrm{\textit{t}\text{-}Bu_3P}$ with $\mathrm{PtCl_2(NCPh)_2}$ in benzene,[6] although the same reaction in dichloromethane gave the chloro-bridged dimer $\mathrm{[PtCl(P\text{-}C)]_2}$ (**2**). Here we discuss possible reaction routes leading to complexes **1** and **2**, as well as the preparation from **2** of several complexes of the type PtCl(P-C)L, L = unidentate ligand.

Results and Discussion

When $\mathrm{\textit{t}\text{-}Bu_3P}$ is allowed to react with $\mathrm{PtCl_2(NCPh)_2}$ in a 2:1 molar ratio in dichloromethane, a mixture of $\mathrm{[PtCl(\textit{t}\text{-}Bu_2PCMe_2CH_2)(\textit{t}\text{-}Bu_3P)]}$ (**1**), $\mathrm{[PtCl(\textit{t}\text{-}Bu_2PCMe_2CH_2)]_2}$ (**2**), and $\mathrm{\textit{t}\text{-}Bu_3PHCl}$ (**3**) is quickly obtained. The reactions described by eq 2–5 are probably involved, leaving eq 1 as the description of the overall reaction.

$$\mathrm{P\text{-}\textit{t}\text{-}Bu_3 + 2PtCl_2(NCPh)_2 \rightarrow [PtCl(\textit{t}\text{-}Bu_2PCMe_2CH_2)(\textit{t}\text{-}Bu_3P)] + [PtCl(\textit{t}\text{-}Bu_2PCMe_2CH_2)]_2 + \textit{t}\text{-}Bu_3PHCl} \quad (1)$$

$$\mathrm{\textit{t}\text{-}PBu_3 + PtCl_2(NCPh)_2 \rightarrow Pt(P\text{-}\textit{t}\text{-}Bu_3)(NCPh)Cl_2 + NCPh} \quad (2)$$

$$\mathrm{Pt(P\text{-}\textit{t}\text{-}Bu_3)(NCPh)Cl_2 \rightarrow {}^1/_2[Pt(P\text{-}\textit{t}\text{-}Bu_2C(CH_3)_2CH_2)Cl]_2 + HCl + NCPh} \quad (3)$$

$$\mathrm{\textit{n}P\text{-}\textit{t}\text{-}Bu_3 + \textit{n}HCl \rightarrow \textit{n}\,\textit{t}\text{-}Bu_3PHCl} \quad (4)$$

$$\mathrm{(1 - \textit{n})P\text{-}\textit{t}\text{-}Bu_3 + {}^1/_2(1 - \textit{n})[Pt(P\text{-}\textit{t}\text{-}Bu_2C(CH_3)_2CH_2)Cl]_2 \rightarrow (1 - \textit{n})PtCl[P\text{-}\textit{t}\text{-}Bu_2C(CH_3)_2CH_2]P\text{-}\textit{t}\text{-}Bu_3} \quad (5)$$

As proof of this, the reactions of eq 2–5 have been carried out independently and found to give the expected products. For example, when $\mathrm{\textit{t}\text{-}Bu_3P}$ and $\mathrm{PtCl_2(NCPh)_2}$ are allowed to react in a 1:1 molar ratio in $\mathrm{CH_2Cl_2}$, the complex $\mathrm{PtCl_2(NCPh)(\textit{t}\text{-}Bu_3P)}$ (**4**) is obtained. In addition, small amounts of complexes **2** and **3** along with unreacted $\mathrm{PtCl_2(NCPh)_2}$ are recovered, suggesting a slow conversion of **4** into **2** (as shown by eq 3). The rate of this conversion of complex **4** into **2** can

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(1) G. W. Parshall, *Acc. Chem. Res.*, **3**, 139 (1970); **8**, 113 (1975), and references therein.

(2) C. E. Jones, B. L. Shaw, and B. L. Turtle, *J. Chem. Soc., Dalton Trans.*, 992 (1974); H. D. Empsall, P. N. Heys, and B. L. Shaw, *ibid.*, 257 (1978), and references therein.

(3) A. J. Cheney and B. L. Shaw, *J. Chem. Soc. A*, 754, 860 (1972).

(4) A. J. Cheney, B. E. Mann, B. L. Shaw, and R. M. Slade, *J. Chem. Soc. A*, 3833 (1971).

(5) R. Mason, M. Textor, N. Al-Salem, and B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, 292 (1976).

(6) R. G. Goel and R. G. Montemayor, *Inorg. Chem.*, **16**, 2183 (1977).

(7) H. C. Clark, A. B. Goel, R. G. Goel, and W. O. Ogini, *J. Organomet. Chem.*, **157**, C16 (1978).

(8) H. C. Clark, A. B. Goel, and S. Goel, *Inorg. Chem.*, in press.

(9) H. C. Clark, A. B. Goel, R. G. Goel, S. Goel, and W. O. Ogini, *Inorg. Chim. Acta*, **31**, L441 (1978).

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