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The electrochemical synthesis of metallocenes, polymethylmetallocenes, 'open metallocenes' and metal phenylacetylides

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Metallocenes, polymethylmetallocenes, metal dimethylpentadienyls and metal phenylacetylides were synthesized by the oxidation of the metal in a solution (acetonitrile, acetonitrile/tetrahydrofuran or acetonitrile/1,2-dimethoxyethane) of the carbon acid C*H (where C* = $PhC{\equiv}C$, C_5H_5, $CH_3C_5H_4$, $(CH_3)_5C_5$, indenyl, fluorenyl and 2,4-dimethylpentadienyl). Metallocenes were extracted with hexane and sublimed *in vacuo*. Metal phenylacetylides precipitated during electrolysis. Current efficiencies indicate Faradaic behaviour. The method provides a significant improvement over the conventional route via alkali metal salts of the carbon acid.

Keywords: Electrochemical, synthesis, metallocene, pentadienyl, phenylacetylide, cyclopentadienyl

INTRODUCTION

This paper describes a direct preparative route to metal derivatives of a variety of carbon acids, here denoted by C*H. In current conventional syntheses, alkali metals are often used to abstract the proton. The pK_a values for the carbon acids used in this study have been found to be: cyclopentadiene 18.1,[1,2] or 18.0;[3] pentamethylcyclopentadiene 26.1;[4] indene 20.1,[5] or 21.0;[6] fluorene 20.5,[7] or 22.6;[8] phenylacetylene 26.4;[7] and 1,3-pentadiene 30.[9]

Conventional preparative methods to a variety of metallocenes have been well described.[10–12] The preparation of 'open metallocenes' follows analogous procedures. Thus a typical preparation of $[Fe(Pl')_2]$ involves proton abstraction from 2,4-dimethylpentadiene (Pl'H) with lithium alkyls followed by reaction with $FeCl_2$ in tetrahydrofuran (THF) at −78°C.[13,14] These bis(pentadienyl) metal complexes are often referred to as 'open metallocenes'.[15] The pentadienyl anion behaves much like a hybrid between cyclopentadienyl and allylic ligands, having both reasonable stability and reactivity.

Several electrolytic preparations of ferrocene have been reported[16,17] which are claimed to be useful as industrial methods. In our hands the method of Ref. 16 has given poor yields; the use of dimethylformamide hampered the separation of the metallocene. Yields of manganese alkyl(aryl)cyclopentadienes near 25% were obtained by the electrolysis of sodium cyclopentadienide and excess alkyl(aryl)cyclopentadiene in THF or pyridine/diethylene glycol dimethyl ether at a manganese anode/copper cathode under a nitrogen atmosphere.[18] More recently, electrolysis at a cobalt anode in dimethylsulphoxide containing cyclopentadiene and a supporting electrolyte gave the cobalticenium cation.[19] Similar preparations of metallocenes to those described in this paper were reported by Grobe *et al.*[20] in 1981. In their work ferrocene was produced in 60% yield and cobaltocene in 50% yield by electrolysis of the metal in a THF solution of [cyclopentadiene(cpH)] and Bu_4NBr for 70 h. No nickelocene was isolated. In 1985 Kumar and Tuck[21] described the one-step electrochemical synthesis of the phenylacetylide of copper (and other metals). Their synthesis was a significant improvement over other methods and is essentially the method described here to generate other metal phenylacetylides.

The aim of this work has been to synthesize a range of organometallic compounds, some of which are of industrial importance, directly from the metal and carbon acid. Comparisons will be made between conventional synthetic methods and the electrochemical route.

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EXPERIMENTAL

General

Iron, cobalt, nickel, copper, zinc, silver and gold (Aldrich, Alfa, BDH and JMC Putatronic; 99.99%) were in the form of rods. A stout platinum sheet (80 mm × 4 mm) formed the inert cathode. Metals were cleaned with 5M hydrochloric acid, then distilled water and ethanol. They were finally polished with fine emery cloth.

Acetonitrile (Ajax) was initially dried over magnesium sulphate, then distilled from P_4O_{10}. Hexane, pentane, diethyl ether (May & Baker) and petroleum ether were dried over sodium wire. Tetrahydrofuran (Ajax) and dimethoxyethane (Hopkins & Wiliams) were freed from alcohol, water and peroxides by treatment with ferrous sulphate heptahydrate, then KOH, and distilled under argon from sodium benzophenone ketyl prior to use.

Dicyclopentadiene (BDH; 99%) and di-(methylcyclopentadiene) (BDH) were thermally cracked at atmospheric pressure and the monomer taken off through a 30-cm double-walled, vacuum-sealed Vigreux column. The monomer was collected in a receiver under argon and cooled to −80°C using an ethyl acetate/liquid nitrogen slush bath. Indene (BDH) was dried over Linde molecular sieves (type 4a). Fluorene (Merck), 2,4-dimethylpentadiene Aldrich), pentamethylcyclopentadiene (Aldrich) and phenylacetylene (Merck) were used as received.

Tetrabutylammonium bromide (Eastman Organic Chemicals), 2,2′-bipyridine (Aldrich) and 1,10-phenanthroline (TCI, Tokyo) were dried *in vacuo* at 80°C/13 Pa and stored in a desiccator. Other reagents were used as supplied.

In practice, solutions and/or their mixtures were distilled under argon into a flask and kept airtight with a rubber septum. Measured quantities were then introduced to the cell with a syringe.

Reaction medium

In a typical series of experiments, a stock solution was made up as follows. The electrolyte (*ca* 200 mg) was added to a 200-cm^3 round-bottom Schlenk flask into which THF and acetonitrile (typically 3:1 ratio) were distilled under argon. Monomeric cyclopentadiene (*ca* 4 cm^3) was then condensed into it (similarly for methylcyclopentadiene). The flask was fitted with a tight rubber septum and maintained at −80°C. Alternatively, 4 cm^3 of $Me_5.C_5H$ or 2,4-dimethylpentadiene was added to the solvent system at room temperature. A syringe was used to deliver measured quantities of the stock solution to the electrolysis cell.

The cell was a 200-cm^3 tall-form beaker with a bottom outlet as described previously.[22-25] The electrodes were immersed into the cell containing a prescribed quantity of solution and electrolysed at ambient temperature at voltages of 40–50 V. A current carrier (*ca* 20 mg) was added to the solution phase since insufficient current flowed in its absence. A voltage of 50 V produced an initial current in any given cell of the order of 15–30 mA. Electrolysis over 1–3 h, as convenient, resulted in the dissolution of approximately 100 mg of metal. In the case of the metallocenes, the organometallic was extracted with hexane, the solvent removed and the complex sublimed *in vacuo* at 80°C/13 Pa. In most cases solutions eventually turned brown. Addition of stannous chloride reduced any cationic species, e.g. $Ni(cp)^+$, to the neutral compound prior to extraction. Complexes which precipitated during electrolysis were collected, washed with ether and were either dried *in vacuo* or over P_4O_{10}. In other preparations, the solution was concentrated by rotary evaporation and the product precipitated with ether. The conditions for the electrochemical preparation of metallocenes and their derivatives are presented in Tables 1 and 2. Conditions for the synthesis of metal phenylacetylides are presented in Table 3.

In the syntheses involving nickel and cyclopentadiene, traces of air led to red or purple solutions, as did insufficiently purified solvents, without, however, lowering the reaction yield appreciably. Similar observations were made by Wilkinson.[22] The compounds were identified by colour, melting point (found to be compatible with literature values), infrared and electronic spectra, microanalysis and nuclear magnetic resonance. Some physiochemical results are presented in Tables 4 and 5.

Reactions meant to produce metallocene carbonyls involved bubbling carbon monoxide gas at atmospheric pressure through the acetonitrile solution containing cpH prior to, and during electrolysis.

Table 1 Electrochemical conditions for the preparation of metallocene compounds and derivatives

		Solution composition[b] (cm^3)				Initial current[c]	Time	Metal dissolved	Yield		
C*H[a]	Metal	MeCN	THF	DME	C*H	(mA)	(min)	(mg)	(mg)	(%)	Product
cpH	Fe	25	—	—	2	150	50	100	233	70	Fe(cp)$_2$
	Ni	20	—	—	1	12	135	29	47	50	Ni(cp)$_2$
	Co	25	—	—	1	30	50	28	58	63	Co(cp)$_2$
	Zn	30	—	—	2	25	85	35	61	58	Zn(cp)$_2$
	Cu	30	+ 100 mg	PPh$_3$	1	50	150	62	198	52	cpCu.PPh$_3$
cpH	Fe	10	25	—	1.5	46	40	38	93	69	Fe(cp)$_2$
	Ni	10	25	—	1	38	40	29	50	51	Ni(cp)$_2$
	Cu	10	25[e]	—	1	21	20	23	78	55	cpCu.PPh$_3$
cpH	Fe	15	—	15	1	58	75	31	72	70	Fe(cp)$_2$
	Ni	5	—	20	1	10	64	11	27	72	Ni(cp)$_2$
MecpH	Fe	5	30	—	1	15	55	12	30	66	Fe(Mecp)$_2$
	Ni	5	30	—	1	24	50	25	65	70	Ni(Mecp)$_2$
Me$_5$C$_5$H	Fe	25	—	—	2	40	60	39	158	69	(Me$_5$C$_5$)$_2$Fe
	Ni	20	—	—	2	18	90	40	87	38	(Me$_5$C$_5$)$_2$Ni
	Co	20	—	—	2	22	80	30	120	71	(Me$_5$C$_5$)$_2$Co
	Zn	30	—	—	0.5	40	60	41	137	65	(Me$_5$C$_5$)$_2$Zn
Pl′H	Fe	5	—	20	0.5	28	75	31	93	68	Fe(Pl′)$_2$
	Ni	5	—	20	0.5	23	50	17	[d]		Ni(Pl′)$_2$
	Co	5	—	25	1	27	60	21	81	49	[Co(Pl′)$_2$]$_2$
	Zn	30	—	—	1	30	80	48	87	45	Zn(Pl′)$_2$
Fluorene	Fe	5	20		0.1 g	62	30	26	115	63	Fe(fluorenyl)$_2$
	Ni	5	15		0.1 g	11	80	15	51	52	Ni(fluorenyl)$_2$
Indene	Fe	5	15		1	29	85	40	112	55	Fe(indenyl)$_2$

[a] C*H refers to carbon acid. [b] Plus 20 mg Bu$_4$NBr. [c] Set at 50 V. [d] Not recorded. [e] Plus 200 mg PPh$_3$.

Table 2 Electrochemical preparation of organocobalt salts

	Solution composition (cm^3)				Initial voltage	Initial current	Time	Metal dissolved	Yield		
C*H[a]	MeCN[b]	THF	C*H	HX[f]	(V)	(mA)	(min)	(mg)	(mg)	(%)	Product
cpH	30[b]	—	1	1	40	20	55	15	131	68	[cp$_2$Co]$_2$CoBr$_4$
	25	—	1	1	40	25	65	18	104	59	[cp$_2$Co]$_2$CoCl$_4$
	5[c]	25	1	—	50	45	70	42	121	63	[cp$_2$Co]Br
Pl′H	25[b]	—	11	30	21	52	23	140	41		[Pl′$_2$Co]$_2$CoBr$_4$
	5[d]	30	11	50	65	60	30	65	38		[Pl′$_2$Co]BF$_4$
Me$_5$C$_5$H	5[e]	25	0.5		50	28	30	12	124	76	[(Me$_5$C$_5$)$_2$Co]$_2$PF$_6$
		+200 mg KPF$_6$									
	30[c]	—	0.5		50	28	60	29	133	66	[(Me$_5$C$_5$)$_2$Co]Br

[a] C*H refers to carbon acid. [b] Plus 20 mg Bu$_4$NBr. [c] Plus 100 mg Bu$_4$NBr. [d] Plus 100 mg Bu$_4$BF$_4$. [e] Plus 200 mg KPF$_6$. [f] HX refers to concentrated aqueous acid.

Table 3 Electrochemical preparation of metal phenylacetylides and their adducts

	Solution composition							Yield		
Metal	MeCN[a] (cm^3)	$\mathrm{PhC{\equiv}CH}$ (cm^3)	N–N[b] (mg)	Initial voltage (V)	Initial current (mA)	Time (min)	Metal dissolved (mg)	(mg)	(%)	Complex
Cu	25	1	—	30	20	30	25	60	92	$\mathrm{PhC{\equiv}CCu}$
Cu	25	1	100	30	19	50	20	130	87	$\mathrm{PhC{\equiv}CCu.phen}$
Ag	25	1	—	30	25	30	60	90	78	$\mathrm{PhC{\equiv}CAg}$
Ag	25	1	100	30	28	30	55	180	74	$\mathrm{PhC{\equiv}CAg.phen}$
Ag	25	1	100	40	8	25	11	20	87	$\mathrm{PhC{\equiv}CAg.bipy}$
Au	25	1	—	30	20	40	25	36	95	$\mathrm{PhC{\equiv}CAu}$
Au	25	1	100	40	13	60	37	50	55	$\mathrm{PhC{\equiv}CAu.phen}$
Au	25	1	100	40	30	46	91	197	76	$\mathrm{PhC{\equiv}CAu.PPh_3}$
Fe	25	1	—	40	17	60	20	72	80	$\mathrm{(PhC{\equiv}C)_3Fe}$
Fe	25	1	200	40	13	30	25	140	71	$\mathrm{(PhC{\equiv}C)_2Fe.phen}$
Fe	20	1	200	40	10	50	34	150	59	$\mathrm{(PhC{\equiv}C)_2Fe.bipy}$
Fe	20	0.5	200	50	46	60	45	175	56	$\mathrm{(PhC{\equiv}C)_2Fe.terpy}$
Ni	20	1	—	40	12	55	12	36	66	$\mathrm{(PhC{\equiv}C)_2Ni}$
Ni	25	1	1 cm^3 [c]	50	15	90	40	489	36	$\mathrm{(PhC{\equiv}C)_2Ni.2(nBu_3P)}$
Co	20	0.5	—	50	26	50	21	57	62	$\mathrm{(PhC{\equiv}C)_3Co}$
Zn	30	1	—	50	60	105	123	390	78	$\mathrm{(PhC{\equiv}C)_2Zn}$
Zn	25	1	100	50	32	90	52	179	53	$\mathrm{(PhC{\equiv}C)_2Zn.bipy}$
Zn	25	1	100	50	44	45	45	178	58	$\mathrm{(PhC{\equiv}C)_2Zn.phen}$

[a] Plus 20 mg Et_4NBr. [b] Refers to heterocyclic amine. [c] nBu_3P used instead of *N*-heterocycle.

Analyses

Microanalytical data were obtained from AMDEL, Victoria, Australia; Analytical Laboratories, Engelskirchen, Germany; and the University of Otago, New Zealand.

Metal content, other than gold and silver, was determined by atomic absorption spectroscopy. Complexes were digested with a 2:1 mixture of concentrated nitric and hydrochloric acids and the solutions of free metal ions made up with Millipore-Q water. AAS standards (BDH; 1.00 cm$^3 \equiv 1$ g litre^{-1}) $FeCl_3$, $CoCl_2$, $NiCl_2$, $CuCl_2$ and $Zn(OAc)_2$ were used to obtain standard curves. Complexes of silver were wet-washed with a mixture of nitric and sulphuric acids and the residue taken up in dilute nitric acid. The silver content was determined potentiometrically.[23] Gold-containing complexes were decomposed with aqua regia, evaporated to dryness, the residue taken up in dilute hydrochloric acid and the gold content estimated gravimetrically.[23] Halogen (Cl^- or Br^-) was estimated potentiometrically using standardized 0.02 M $AgNO_3$. Complexes were dissolved in moderately concentrated nitric acid and solutions made up with Millipore-Q water.

Instrumentation

The electrolysis was controlled by a Bang & Olufsen SN15 power supply delivering up to 50 V (dc) and 1 A.

Potentiometric titrations were performed using a Radiometer Copenhagen PHM62 Standard pH meter with Ag/AgCl and saturated calomel electrodes.

Atomic absorption spectroscopy was conducted on a Varian Model AA 1235 series spectrometer with Fe (Phototron), Co (Phototron), Ni (S&N Juniper & Co.), Cu (Varian) and Zn (S&N Juniper & Co.) cathode lamps.

Infrared spectra were recorded in the region 5000–330 cm^{-1} using a Jasco A:302 spectrophotometer and in the far-infrared region on a Perkin–Elmer 457 instrument, both calibrated with a polystyrene film. Samples were in the form of potassium bromide discs.

Solution electronic spectra were recorded in the range 190–850 nm at 25°C on a Hitachi Model 150:20 double-beam spectrophotometer.

Diffusion reflectance spectra were recorded over the range 300–2500 nm on a Beckman DK-2A ratio recording spectrophotometer using spectroscopic-grade barium sulphate in the reference beam.

Nuclear magnetic resonance spectra were run by the University of Melbourne Chemistry Department's NMR service and recorded on the JEOL FX-90 and FX-100 spectrometers: ^1H was measured at 100 MHz and resonances referenced against trimethylsilyl (TMS).

RESULTS AND DISCUSSION

For the metallocenes and their analogues the synthetic conditions are summarized in Tables 1 and 2 and some of the features of the compounds including analyses are listed in Table 4. In contrast with some previously reported methods, dimethylformamide (DMF) was not used in the syntheses described here. Although DMF provides good electrical conductivity it has a high boiling point and a low vapour pressure, making recovery of the end product difficult. Similarly dimethyl sulphoxide was not used.

Table 4 Physiochemical results for the metallocenes, polymethylmetallocenes and metal dimethylpentadienyls

Organometallic	Colour	M.pt (°C)	Metal (calcd) (%)
$Fe(cp)_2$[a]	Orange	173	29.9 (30.0)
$Ni(cp)_2$[b]	Green	172–173	30.9 (31.0)
$Co(cp)_2$	Dark violet	173	30.9 (31.2)
$Zn(cp)_2$	White	185–187	33.0 (33.4)
$cpCu.PPh_3$	Olive brown	>250	16.6 (16.3)
$[Co(cp)_2]Br$	Green	>250	21.9 (21.9)
$[Co(cp)_2]_2[CoCl_4]$[c]	Grass green	>300	30.3 (30.5)
$[Co(cp)_2]_2[CoBr_4]$[d]	Yellow–green	>300	23.2 (23.4)
$Fe(Mecp)_2$	Orange	37–39	26.2 (26.1)
$Ni(Mecp)_2$	Dark green	36–38	27.2 (27.1)
$Fe(Me_5C_5)_2$	Yellow	292–295	17.0 (17.2)
$Ni(Me_5C_5)_2$	Olive green	284	17.2 (17.8)
$Co(Me_5C_5)_2$	Black	293–295	17.6 (17.9)
$Zn(Me_5C_5)_2$	Pale yellow	>280	18.9 (19.6)
$[Co(Me_5C_5)_2]Br$	Green	>280	14.1 (14.4)
$Fe(indenyl)_2$	Violet–black	186–189	19.2 (19.6)
$Fe(fluorenyl)_2$	Red	178–182	14.3 (14.5)
$Ni(fluorenyl)_2$	Orange–brown	180–183	14.7 (15.1)
$Fe(Pl')_2$	Orange	>250	22.2 (22.7)
$Ni(Pl')_2$	Brown	>250	22.8 (23.6)
$[Co(Pl')_2]_2$	Red/brown	>280	22.7 (23.7)
$Zn(Pl')_2$	White	>250	25.0 (25.6)

[a] Found: C, 64.4; H, 5.48. Calcd: C, 64.6; H, 5.42%. [b] Found: C, 64.5; H, 5.87. Calcd: C, 63.7; H, 5.34%. [c] Found: Cl, 24.0. Calcd: Cl, 24.5%. [d] Found: Br, 42.4. Calcd: Br, 42.3%. Replicate analyses suggest the observed values are accurate ±3% here and in Table 5.

The aim of this work was to establish the applicability of electrolytic synthesis to the preparation of organometallic species. No attempt was made to establish optimum currents or voltages, but the work-up procedures maximized the yield in the metallocene preparations. The overall yields of the organometallic preparations were in the range 38–71% relative to the amount of metal dissolved, with most yields being greater than 50%.

The weakly acid C–H bond in each of the ligands used was easily cleaved electrolytically to produce the required anion. As the pK_a increases, it becomes progressively more difficult to deprotonate these acids with alkali, whereas electrolytically the rupture of the C–H bond occurs readily. The simple and direct preparations of these compounds is an elegant illustration of the attraction of this synthetic method. In conventional syntheses carbon acids may be metallated using strongly basic lithium regents but varying the metal, as it is so easy to do using the electrochemical technique, opens the way to new synthetic pathways. We may list the advantages of the method as follows;

(i) ambient temperatures rather than thermolytic procedures are used;
(ii) C–H bond rupture occurs by electrical rather than chemical means;
(iii) the electrical potential activates the metal;
(iv) tedious preparations of alkali metal salts of the carbon acids are avoided;
(v) organometallic complexes are produced and isolated in a short time in a state of high purity. Air-sensitive solutions are easily delivered to Schlenk apparatus for further manipulation.

The use of mixed solvent systems (e.g. tetrahydrofuran/acetonitrile) provided good conductivity and produced well crystallized products.

The synthesis of ferrocene by the electrolytic method was straightforward. In previous similar work, Grobe *et al.*[20] used THF as a solvent; the low dielectric constant and poor solvent properties for the electrolyte required long hours of

Table 5 Physiochemical results for the metal phenylacetylides and their adducts

Organometallic	Colour	M.pt (°C)	Metal (Calcd) (%)
$PhC{\equiv}CCu$	Gold	d.190	39.1 (38.6)[a]
$PhC{\equiv}CCu$.phen.	Red–brown	d.130	18.4 (18.4)
$PhC{\equiv}CAg$	Off-white	d.185	51.6 (52.1)
$PhC{\equiv}CAg$.phen	Light grey	175–180	25.9 (26.5)
$PhC{\equiv}CAg$.bipy	Beige	185–187	29.0 (29.5)[b]
$PhC{\equiv}CAu$	Yellow	d.180	65.4 (66.1)
$PhC{\equiv}CAu$.phen	Light brown	95–97	39.1 (39.7)
$PhC{\equiv}CAu.PPh_3$	Beige	115–117	34.7 (35.2)
$(PhC{\equiv}C)_3Fe$	Brown	>260	15.7 (15.6)
$(PhC{\equiv}C)_2Fe$.phen	Dark purple	65–67	12.4 (12.7)
$(PhC{\equiv}C)_2Fe$.bipy	Dark red	d.150	13.7 (13.5)
$(PhC{\equiv}C)_2Fe$.terpy	Purple	110–112	10.9 (11.4)
$(PhC{\equiv}C)_2Ni$	Brown	>260	21.9 (22.4)
$(PhC{\equiv}C)_2Ni.2\ (nBu_3P)$	Orange	65–68	7.9 (8.8)
$(PhC{\equiv}C)_3Co$	Green	>200	16.5 (16.3)
$(PhC{\equiv}C)_2Zn$	Off-white	>250	24.3 (24.4)
$(PhC{\equiv}C)_2Zn$.bipy	Cream	>260	15.0 (15.4)
$(PhC{\equiv}C)_2Zn$.phen	Beige	d.200	14.4 (14.6)

[a] Found: C, 58.4; H, 3.07. Calcd: C, 58.4; H, 3.06%. [b] Found: Cu, 59.0; H, 3.41; N, 7.42. Calcd: 59.2; H, 3.58; N, 7.67%.

reaction and copious quantities of electrolyte. The use of acetonitrile or a mixed solvent system containing acetonitrile increased the dielectric constant and greatly reduced reaction times. It is worth noting that when iron was oxidized in acetonitrile containing cyclopentadiene and a quantity of bromine, only ferrous bromide was isolated.

The preparation of cobaltocene and nickelocene required anaerobic procedures; prolonged electrolysis in the case of nickel led to the formulation of brown cp_2Ni^+. White polymeric[24] cp_2Zn was easily prepared, as was the copper species $[cpCuPPh_3]$ by the prior addition of triphenylphosphine. The latter compound was first prepared by Piper and Wilkinson.[25] Carbon monoxide at 1 atm pressure failed to produce metallocene carbonyls. Grobe *et al.*[20] required much higher pressures for such reactions to proceed. The addition of small quantities of concentrated aqueous HX (X = Cl or Br) or of an excess of electrolyte produced the cobalt salts listed in Table 2 and $[M(Me_5C_5)_2]PF_6$ (M = Fe or Ni). These compounds were characterized by analysis as well as by infrared, electronic and NMR spectroscopy and by magnetic measurements. The $[M(Me_5C_5)_2]PF_6$ compounds are soluble in acetone and acetonitrile, sparingly soluble in THF and ether, and insoluble in aliphatic hydrocarbons. The cationic iron, cobalt and nickel compounds are air-stable solids but the nickel complex is air-sensitive in solution. Similarly, the $[Co(Me_5C_5)_2]BF_4$ complex was made by the prior addition of $[NH_4BF_4]$ to the electrolysis solution and is a brick-red solid. The bis(cobalticenium) tetrahalocobaltate(II) salts were prepared in one step by the addition of a small quantity of concentrated acid to the solution phase. The products are air-stable green compounds insoluble in ether. This preparation is superior to that of van den Akker and Jellinek,[26] who first prepared cobaltocene then reacted it with the acids. The $[Co(Me_5C_5)_2]PF_6$ salt is a green powder.

The neutral decamethylmetallocenes were isolated from their solutions with pentane. They melt in the range 290–300°C and are volatile, subliming at temperatures greater than 70°C/13 Pa. The iron species is yellow, the nickel olive-green and the cobalt black. With the exception of $[Fe(Me_5C_5)_2]$, the neutral compounds are air-sensitive both as solids and in solution. Like the First Transition Series metallocenes, the permethylated compounds undergo facile one-electron oxidation to isolable monocationic derivatives.[27]

The open-chain pentadienes are much less acidic than the cyclic compounds, but the syntheses of the metal compounds proceeded equally smoothly.

Coinage metal compounds, especially acetylenic derivatives of copper, are extensively used in organic synthesis. Kumar and Tuck[21] recently suggested the electrolytic route as a simple one-step route to copper acetylide and other compounds. The compounds listed in Table 3 confirm the generality of this direct method. The presence of bipyridyl or 1,10-phenanthroline in the electrolysis medium produced adducts of the organometallic compound, but when terpyridyl, picolylamine, triphenylphosphine or excess Bu_4NBr were presented in solutions containing phenylacetylene, electrolysis at a copper anode produced only $[PhC{\equiv}CCu]$. However, electrolysis at a gold anode in the presence of triphenylphosphine and phenylacetylene produced $[PhC{\equiv}CAu \cdot PPh_3]$.

The characterization of the products was mainly by metal analysis and by the use of infrared spectra (see below); analytical results are listed in Tables 4 and 5.

Reaction mechanism

In the present systems, the measured current efficiencies were all less than 1.2 mol F^{-1}. These results imply that the electrode processes of the metal, M, and carbon acid, C*H (where C* = cp, Mecp, Me_5C_5, Pl′, PhC≡C), are as follows:

$$\text{Cathode:}\quad ne^- + n(C^*H) \rightarrow n(C^*)^- + \frac{n}{2}H_2(g)$$

$$\text{Anode:}\quad M \rightarrow M^{n+} + ne^-$$

$$\text{Overall reaction:}\quad M^{n+} + n(C^*)^- \rightarrow M(C^*)_n$$

for which the overall E_f should be equal to $1/n$. These results are in good agreement with the mechanism outlined above, as is the visible production of hydrogen gas at the cathode. The simplicity of the mechanism suggests that this technique finds general application in the syntheses of organometallic complexes involving anionic ligands derived from carbon acids.

Infrared spectra

A major characterization method for the products was their infrared spectra; a brief discussion of these spectra follows. The infrared spectra of the metallocenes were identical to those in the literature.[28] In addition to the C–H stretching frequency at 3075 cm^{-1}, bands at 1002 and 811 cm^{-1} in ferrocene arise from C–H bending vibrations. The absorption at 1411 cm^{-1} is an antisymmetric C–C stretching vibration and the band at 1108 cm^{-1} is an antisymmetric ring breathing mode. The infrared spectra of $[cp_2Co]_2[CoX_4]$ are similar to the spectra of the cobalticenium salts.[28] Infrared spectra for the iron–fluorenyl and $[cp_2CoPF_6]$[21] complexes were identical with those described in the literature.

The introduction of methyl substituents onto the cyclopentadienyl ring lowers the C–H stretching frequency to 3000–3100 cm^{-1}. The symmetric vibrations occur in the range[29] 1385–1375 cm^{-1}. Otherwise, few great changes occur in the spectra of decamethylmetallocenes compared with the metallocenes. The spectra of the compounds reported here were identical with those recorded in the literature.[29]

The infrared spectrum of $[Zn(Me_5C_5)_2]$ contains two medium-to-strong absorption bands at 450 and 340 cm^{-1} which are assigned to metal–ring stretching modes.[30] The lower frequency band overlaps with ring deformation modes. A doubling of a majority of the ring and $C{-}CH_3$ modes between 1450 and 600 cm^{-1} is consistent with the presence of two differently bonded ligand rings. The highest C_5 ring mode is found at 1652 cm^{-1}, virtually unchanged from Me_5C_5H, and is assigned to an η^1-bonded ring with localized single and double bonds.[30]

The infrared spectra of the cationic complexes are similar but more poorly resolved. Since these bands are insensitive to changes in metal ion oxidation state and even geometry, they must represent primarily ligand vibrational modes for the η^5-bound Me_5C_5-moiety.[31a] Below 600 cm^{-1}, where metal–ring vibrations are expected to occur, the infrared spectra vary from complex to complex.

The infrared spectrum of bis(2,4-dimethylpentadienyl)iron(II) lacks absorptions due to C═C bonds although 'aromatic' C—C bands can

Table 6 Nuclear magnetic resonance data for the organometallic compounds prepared

Complex	Solvent	^{1}H resonances, δ (ppm)	Ref.
$Fe(cp)_2$	CCl_4	4.04	37
$Fe(cp)_2$	$CDCl_3$	4.19s	This work
$[cp_2Co]_2[CoCl_4]$	DMSO-d_6	5.13br	This work
$[cp_2Co]_2[CoBr_4]$	DMSO-d_6	5.48br	This work
Fe(fluorenyl)$_2$	$CDCl_3$	3.37d, 1.86s, 1.5d, 1.25s, 1.024t	This work
Fe(indenyl)$_2$	$CDCl_3$	6.50s, 4.45d, 4.96t	This work
$Fe(Pl')_2$	C_6D_6	4.40s, 2.68s, 1.85s, 0.26	13
$Fe(Pl')_2$	$CDCl_3$	4.21s, 2.40s, 1.56s, 0.11	This work
$Fe(Me_5C_5)_2$		1.62s	29
$Fe(Me_5C_5)_2$	C_6D_6	1.70s	12
$Fe(Me_5C_5)_2$	$CDCl_3$	1.55s	This work
$Zn(Me_5C_5)_2$		1.98	30
$Zn(Me_5C_5)_2$	$CDCl_3$	1.95	This work
$[(Me_5C_5H)_2Co]PF_6$	Acetone-d_6	1.78	This work
$PhC\equiv CCu$	$CDCl_3$	1.53s, 7.01–7.5 m	This work
$PhC\equiv CAg$	$CDCl_3$	1.55s, 7.0–7.3 m	This work
$PhC\equiv CAu$	$CDCl_3$	1.57s, 7.2–7.3 m	This work
$(PhC\equiv C)_3Co$	$CDCl_3$	7.1–7.4 m	This work
$PhC\equiv CCu$.phen	$CDCl_3$	1.48s, 7.2–8.5 m	This work
$PhC\equiv CAg$.phen	$CDCl_3$	1.69s, 7.26s, 7.59–9.25 m	This work
Indene		1.95s, 3.27s, 6.38–7.42 mult.	38
Fluorene		2.091s, 3.27s, 7.2–7.79 mult.	38
Me_5C_5H		0.96d, 1.75s	38
Me_5C_5Na	THF-d_8	2.01	12
2,4-Dimethylpentadiene		1.87s, 4.8d, 5.65s	38
$PhC\equiv CH$		3.1s, 7.35–7.7 m	38
1,10-Phenanthroline		7.7–9.25 m	38

be observed, consistent with η^5 coordination.[12] The infrared contains a band near 1480 cm^{-1} that is typical of π-allyl compounds. Similar observations are made for the other analogues. In all cases the spectra of the compounds reported have agreed well with literature spectra.

The interpretation of the infrared spectra of the metal acetylides and their adducts was aided by the work of Garbuzova and co-workers[31] and of King and So.[32] The spectra of the acetylides reported here agree well with those in the literature; the ligand bands for phenanthroline, bipyridyl, triphenylphosphine, terpyridyl and *n*-butylphosphine confirm the formation of the adducts listed in Table 5.

Magnetic studies

The observed magnetic moments of 4.7 Bm (Bohr magnetons) (chloro) and 4.8 Bm (bromo) for the $[cp_2Co]_2[CoX_4]$ (where $X = Cl$, Br) salts are ascribed to high-spin tetrahedral coordination while the cobalt(III) atom in the cobalticenium ion will be spin-paired. The increase in the moment of the $[CoX_4]^{2-}$ ion will be spin-paired. The increase in the moment of the $[CoX_4]^{2-}$ ion in the sequence $Cl < Br$ indicates an increasing contribution by spin-orbit coupling, in agreement with the spectrochemical series.[33]

Electronic spectra

The major electronic bands in the spectra of the metallocenes, decamethylmetallocenes and open metallocenes are identical to those reported.[12] For $[Co(Me_5C_5)_2]PF_6$ shoulders found at 420, 335 and 200 nm are assigned to the three spin-allowed transitions $^1A_{1g} \rightarrow {}^1E_{1g}(a)$, $^1E_{2g}$ and $^1E_{1g}(b)$.[31a] Diffuse reflectance revealed three weak absorptions at 785, 540 and 460 nm assigned to the three spin-forbidden ligand field transitions. A weak but sharp peak is found at 1190 nm due to a vibrational overtone. The spectrum of $[Fe(Me_5C_5)_2]$ exhibits only two bands (425 and 325 nm), the intensity of which suggests a ligand-field origin. The spectrum of $[Ni(Me_5C_5)_2]^+$ consists of a weak absorption at 440 nm assigned to the $^1A_{1g} \rightarrow {}^1E_{1g}$(a) transition, intense peaks at 317 and 244 nm and a shoulder at approximately 235 nm.

The electronic spectra of the compounds $[cp_2Co]_2[CoX_4]$, where X = Cl, Br, are consistent with the presence of tetrahedral configurations,[33] with the maximum near 400 nm being due to the cobalticenium cation.[12]

Nuclear magnetic resonance spectra

Resonances for the free carbon acids and their compounds are found in Table 6. A single, sharp singlet is observed in the proton NMR spectrum of the decamethylmetallocenes arising from the 15 equivalent methyl protons. This contrasts with the four vinylic methyl groups and the one allylic methyl group apparent in the spectrum of free Me_5C_5H.[34] The single peak found at 1.95 ppm in the proton spectrum of $[Zn(Me_5C_5)_2]$ is the result of the rapid exchange at the η^1- and η^5-bonded rings.[30] In the solutions of $[cp_2Co]_2[CoX_4]$ (where X = Cl, Br), proton signals of the $[cp_2Co]^+$ cation are shifted to higher fields and are broadened. This is due to the presence of labile ion pairs in these solutions which cause the signal to be shifted and broadened by pseudocontact interactions with the paramagnetic anion.[35]

^{1}H NMR spectra for $[Fe(Pl')_2]$ are consistent with the formulation of these complexes as 'open sandwiches'. For this symmetrical complex, four resonances are observed, indicating equivalent ligands in which an apparent vertical mirror plane of symmetry (perpendicular to the ligand plane) is present.[36] Variable-temperature ^{13}C NMR[37] confirmed the *gauche*-eclipsed conformation.

CONCLUSION

Successful one-step preparations of a range of metallocenes, polymethylated metallocenes, 'open metallocenes' and metal phenylacetylides were achieved directly from the metal and carbon acid in acetonitrile (MeCN), tetrahydrofuran/MeCN or dimethoxyethane/MeCN. The weak C–H bond was cleaved by electrical means rather than by alkali. Use of these procedures was far superior to the conventional use of the alkali salt of the diene. Products were of excellent purity and crystallinity.

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