A new synthetic route to functionally substituted (η⁵-cyclopentadienyl) dicarbonyliridium compounds ☆

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Abstract

A series of functionally substituted (η⁵-cyclopentadienyl)dicarbonyliridium compounds have been prepared from reactions of the corresponding substituted cyclopentadienyl-sodium, -lithium, or -thallium reagents with chlorodicarbonyl(pyridine)iridium. Ring-substituted compounds synthesized by this route include chloro, benzyl, pentabenzyl, acetyl, carbomethoxy, methyl, benzoyl, trimethylsilyl, cyano, dimethylamino, tetraphenyl, dimethylaminoethyl, (tetramethyl)dimethylaminoethyl, methoxyethyl and pentamethyl. The symmetric and asymmetric carbonyl stretching frequencies as well as the ¹³C NMR chemical shifts of the carbonyl substituents have been correlated with various Hammett substituent parameters.
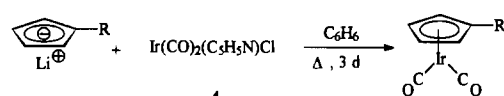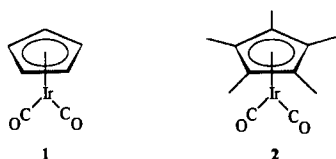
1. Introduction

Interest in developing a new, less expensive, high-yield synthetic route to ring-substituted (η⁵-cyclopentadienyl)dicarbonyliridium compounds stems from their potential utility as C—H bond activation intermediates. Rausch and coworkers were the first to demonstrate that organoiridium compounds could insert into C—H bonds [1]. They found that photolysis of a benzene solution of (η⁵-cyclopentadienyl)dicarbonyliridium (1) and photo-2-pyrone unexpectedly led to the organoiridium products (η⁵-C₅H₅)(CO)Ir(C₆H₅)H and (η⁵-C₅H₅)₂(CO)₂Ir₂(C₆H₄), resulting from oxidative addition of the C—H bonds of benzene to a photoactivated form of 1. Subsequent studies by Hoyano and Graham [2] demonstrated that photolysis of (η⁵-C₅Me₅)Ir(CO)₂ (2) in alkane solvents such as neopentane and cyclohexane generated the corresponding alkyl hydrido compounds (η⁵-C₅Me₅)(CO)Ir(R)H (R = neopentyl or cyclohexyl), formed by oxidative addition of unactivated sp³ C—H bonds to iridium. An independent but related investigation by Janowicz and Bergman [3] found that irradiation of the dihydrido compound (η⁵-C₅Me₅)(PMe₃)IrH₂ in benzene or alkane solvents resulted in extrusion of H₂ and the formation of the products (η⁵-C₅Me₅)(PMe₃)Ir(R)H (R = phenyl, neopentyl, cyclohexyl), again resulting from oxidative addition of sp² or sp³ C—H bonds to a photochemically-generated coordinatively unsaturated intermediate.

It would be of considerable interest to examine the effects of other ring substituents on reactions of this type, since both intra- and inter-molecular C—H bond insertions might be expected to occur. Unfortunately, compounds of this type are currently unknown. However, recent studies in our laboratory have demonstrated that a wide variety of functionally-substituted organoiridium compounds of the type (η⁵-C₅H₄R)(CO)(PPh₃)Ir, where R = alkyl, acyl, chloro, dimethylamino, etc., can be prepared from reactions of the corresponding cyclopentadienyl-thallium, -sodium, or -lithium reagents with *trans*-chlorocarbonylbis(triphenylphosphine)iridium [4]. We have subsequently developed a new synthetic route to ring-substituted (η⁵-cyclopentadienyl)dicarbonyliridium compounds, and these findings together with results of Hammett-type substituent correlation studies are described in the present paper. Investigations of these compounds as

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1

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Scheme 1.

R =			
$(CH_3)_5$		3	84%
CH_3		5	74%
$Si(CH_3)_3$		6	94%
$(CH_2C_6H_5)_5$		8	8%
$(C_6H_5)_4$		9	35%
$(CH_2)_2N(CH_3)_2$		10	45%
$(CH_3)_4(CH_2)_2N(CH_3)_2$		11	92%
$(CH_2)_2OCH_3$		12	27%

precursors for C—H bond activation are in progress and will be reported in subsequent publications.

2. Results and discussion

Previous synthetic routes to **2** and related organoiridium compounds such as $(\eta^5\text{-}C_5Me_5)(PMe_3)IrH_2$ have been based on earlier studies by Maitlis et al. [5], starting with hexamethylbicyclo[2.2.0]hexadiene [hexamethyl(Dewar benzene)] and iridium trichloride hydrate, and involving several additional transformations. This route is therefore limited in scope. On the other hand, the parent compound **1** has been prepared in good yield from reactions of either cyclopentadienyl-sodium [6] or -thallium [7] with chlorotricarbonyliridium, and we have also shown that a reaction of this iridium reagent and vinylcyclopentadienyllithium affords $(\eta^5\text{-}$vinylcyclopentadienyl)dicarbonyliridium in high yield [8].

While chlorotricarbonyliridium is a potentially useful intermediate for preparing functionally-substituted $(\eta^5\text{-}$cyclopentadienyl)dicarbonyliridium compounds, it can only be prepared by the tedious and lengthy carbonylation of iridium salts [6,9], is polymeric and relatively insoluble in organic solvents, and is very expensive if obtained commercially. In contrast, the related compound chlorodicarbonyl(p-toluidine)iridium, $IrCl(CO)_2$-$(p\text{-}CH_3C_6H_4NH_2)$ (**3**), is readily synthesized in the laboratory in high yield [10] and Bitterwolf et al. [11] have recently demonstrated its synthetic utility in the formation of bis[$(\eta^5\text{-}$cyclopentadienyl)dicarbonyliridium]methane.

Our initial studies using **3** as a precursor in organoiridium chemistry were disappointing. Attempted synthesis of **1** from reactions of this reagent with either cyclopentadienyl-sodium or -lithium gave ca. 5% crude yields of the desired product contaminated with p-toluidine. An analogous reaction of **3** with cyclopentadienylthallium produced **1** in 34% yield; however, the product had to be chromatographed on alumina to remove the p-toluidine byproduct.

It seemed possible that the poor yields of **1** in these reactions could result from the preferential metalation of the amino group of **3** by the metal cyclopentadienide reagent, instead of the desired nucleophilic attack on iridium which would lead to **1**. We next investigated chlorodicarbonyl(pyridine)iridium (**4**) as a starting ma-
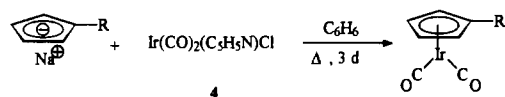
terial, since this compound lacks amino hydrogens, is readily synthesized from chlorodicarbonyl(p-toluidine)iridium (**3**) in high yield [12] and produces a volatile byproduct (pyridine) that can be readily removed under vacuum.

Reactions of **4** with the lithium, sodium and thallium salts of various substituted cyclopentadienyl ligands led to the desired functionally-substituted $(\eta^5\text{-}$cyclopentadienyl)dicarbonyliridium compounds. Byproducts and solvents were readily removed under high vacuum and the reaction residues were extracted with hexane. Subsequent vacuum distillation, vacuum sublimation or crystallization gave the desired products in fairly high yields and high purity. Scheme 1 shows the products obtained using substituted cyclopentadienyllithium reagents and gives the yields for the various reactions. In general, the more thermally sensitive or more sterically hindered the cyclopentadienide, the lower the yield.

Functionally-substituted sodium cyclopentadienides also reacted with **4** to give the desired functionally-substituted analogs of **1** in good yields. Compound **1** itself was obtained in 72% yield by this route, whereas it was obtained in only 5% yield in reactions of cyclopentadienylsodium with **3**. Scheme 2 summarizes the products and yields obtained by this route.
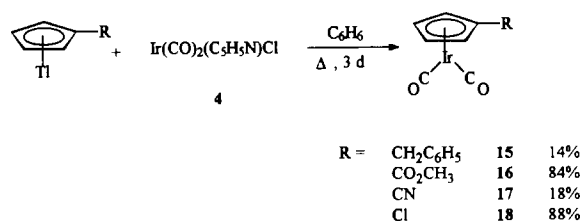
Substituted cyclopentadienylthallium reagents likewise reacted readily with **4** to give the desired products in low to excellent yields. Scheme 3 shows the synthesis and yields of the compounds obtained by this method.

Correlations between the symmetric and asymmetric stretching frequencies of the carbonyl ligands and the Hammett constants for the ring substituents gave highly linear plots, with the best results obtained for σ_{p^0} (see Fig. 1). Table 1 lists the various substituent constants, the corresponding correlation coefficients for the

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R =			
H		1	72%
$C(O)CH_3$		13	62%
$C(O)C_6H_5$		14	31%

Scheme 2.

Scheme 3.

$$R = \quad CH_2C_6H_5 \quad 15 \quad 14\%$$
$$CO_2CH_3 \quad 16 \quad 84\%$$
$$CN \quad 17 \quad 18\%$$
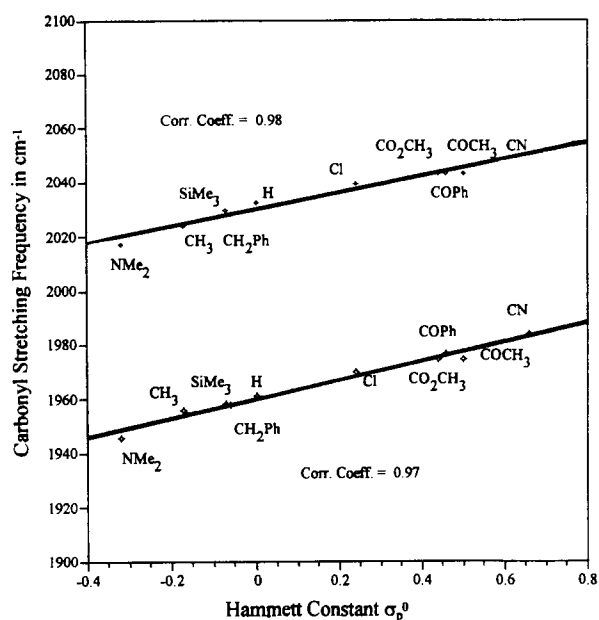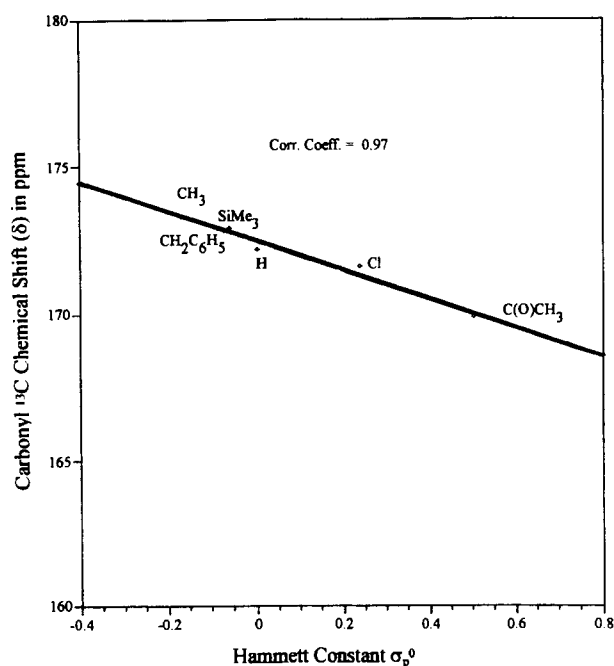$$Cl \quad 18 \quad 88\%$$

Fig. 1. Correlation of carbonyl stretching frequency data with $\sigma_p{}^0$.

Fig. 2. Correlation of ^{13}C NMR carbonyl chemical shift data with $\sigma_p{}^0$.

Table 1
Correlation of substituent parameters with IR and ^{13}C NMR spectral data

Substituent constant [a]	ν_{CO} symmetric correlation coeff.	ν_{CO} asymmetric correlation coeff.	$\delta(^{13}CO)$ correlation coeff.
σ_m	0.90	0.91	0.78
σ_p	0.94	0.94	0.98
σ_p^0	0.97	0.98	0.97
$\sigma_p{}^+$	0.83	0.82	0.96
$\sigma_p{}^-$	0.90	0.93	0.93
F	0.67	0.68	0.65
R	0.63	0.63	0.51

[a] Hammett-type substituent constants obtained from Refs. [14–16].

carbonyl stretching frequencies, and the correlation coefficients for the ^{13}C NMR chemical shifts of the carbonyl ligands. This is the first example reported of Hammett-type correlations of organometallics using the ^{13}C NMR chemical shifts of the metal carbonyl ligands. All of the σ_p variants gave excellent correlations (Fig. 2), indicating definite ring-substituent effects transmitted through the iridium atom to the carbonyl ligands in this series of compounds. The negative slope seen in Fig. 2 is consistent with the observed ^{31}P NMR chemical shifts seen in the functionally-substituted (η^5-cyclopentadienyl)carbonyl(triphenylphosphine)iridium series reported by us previously [4] and in the arene chromium carbonyl system reported by Bitterwolf [13].

3. Experimental details

All operations were carried out under a nitrogen atmosphere using Schlenk tube techniques, except where specified. The nitrogen was deoxygenated using BASF catalyst and dried with P_2O_5 and molecular sieves. Infrared spectra were recorded on a Perkin-Elmer 1600 FT-IR infrared spectrometer. Samples were prepared as CH_2Cl_2 solutions using subtraction techniques to remove solvent signals. ^{1}H and ^{13}C NMR spectra were recorded on IBM NR-80 or Brucker AC-200 spectrometers, respectively. GC-MS data were recorded on an HP 5970A gas chromatograph/mass spectrometer, using an HP-5 column and 1200 eV ionization energy. Solid sample mass spectra (MS) were performed on a VG/Biotech Platform 2 LC–MS, introduced in the solids probe and volatilized at 250°C, at the US Military Academy at West Point, NY. Benzene, pentane, hexane, ethyl ether and tetrahydrofuran (THF) were dried over NaK alloy and distilled under argon. Dichloromethane was dried over and distilled from calcium hydride. Melting points are uncorrected and were determined under nitrogen atmosphere in sealed capillary tubes. Elemental analyses were performed by the Microanalytical Laboratory, University of Massachusetts. Chlorodi-

carbonyl(p-toluidine)iridium (3) was obtained as a purple solid (m.p. 165°C) in 90% yield following a literature procedure [10]. ^{1}H NMR (CDCl$_3$) δ: 7.14 (s, 4H, aromatic); 5.41 (br s, 2H, NH$_2$); 2.35 (s, 3H, CH$_3$) ppm. FT-IR (benzene) (cm^{-1}): 2074.4, 1991.6 (ν_{CO}). Chlorotricarbonyliridium was purchased from Strem Chemicals, Inc.

3.1. Chlorodicarbonyl(pyridine)iridium (4) [9]

Chlorodicarbonyl(p-toluidine)iridium (3) (0.84 g, 2.1 mmol) was dissolved in 180 ml of ethyl ether and pyridine (0.16 ml, 2.0 mmol) in 30 ml of ethyl ether was added dropwise to the stirred solution. The color changed from purple to a yellow–green. The solution was concentrated to ca. 20 ml, 60 ml of hexane was added and the solution placed in a freezer at −15°C overnight. Chlorodicarbonyl(pyridine)iridium (0.70 g, 92% yield, m.p. 73°C) was collected as metallic green, knife-like crystals that were dichroic (when a light was placed behind them they appeared to be purple). ^{1}H NMR (CDCl$_3$) δ: 8.84–8.70 (dd, 2H, aromatic); 8.05–7.85 (m, 1H, aromatic); 7.62–7.48 (t, 2H, aromatic) ppm. FT-IR (THF) (cm^{-1}): 2075, 1981 (ν_{CO}); (KBr pellet) (cm^{-1}): 2072, 1998; (benzene)(cm^{-1}): 2074, 1989.

3.2. (η^5-Cyclopentadienyl)dicarbonyliridium (1)

Method (a)

Chlorodicarbonyl(p-toluidine)iridium (3) (0.40 g, 1.0 mmol) and 0.50 g (5.7 mmol) of cyclopentadienylsodium were refluxed in 50 ml of benzene for 4 d. The solution was allowed to cool and the solvent removed under vacuum. (Heating the solution while removing the solvent can lead to loss of product due to its volatility.) A purple oily residue remained which gave the product as a yellow oil upon microdistillation. However, the oil was contaminated with p-toluidine and the yield (5%) was very low.

Method (b)

Chlorodicarbonyl(pyridine)iridium (4) (0.40 g, 1.1 mmol) and 0.50 g (5.7 mmol) of cyclopentadienylsodium were refluxed in 50 ml of benzene for 4 d. The solution was cooled to room temperature and filtered through a Florisil–Celite plug. The solvent was removed and the residue was microdistilled giving 0.25 g of 2 as a bright golden oil (72% yield). ^{1}H NMR (CDCl$_3$) δ: 5.46 (s, 5H, C$_5$H$_5$) ppm. ^{13}C NMR (CDCl$_3$) δ: 172.19 (CO); 83.88 (C$_5$H$_5$) ppm. FT-IR (CH$_2$Cl$_2$) (cm^{-1}): 2032.8, 1961.3 (ν_{CO}); (neat) (cm^{-1}): 2037, 1957. GC–MS m/e: 314, 312 (M$^+$); 286, 284 (M − CO)$^+$; 258, 256 (M − 2CO)$^+$.

3.3. (η^5-Benzylcyclopentadienyl)dicarbonyliridium (8)

Benzylcyclopentadienylthallium [17] (0.75 g, 2.1 mmol) and 0.31 g (0.85 mmol) of 4 were refluxed in 50 ml of benzene for 3 d. After cooling to room temperature, the solvent was removed under vacuum and the residue extracted with 3 × 20 ml of hexane. The hexane was concentrated to 5 ml and neutral alumina was added. Chromatography on alumina and elution with hexane/methylene chloride (3 : 1) produced a single yellow band. Removal of solvent under vacuum yielded a yellow waxy material which was distilled under vacuum (110°C/1 mmHg) giving a golden yellow oil (0.050 g, 14.4% yield). An analytical sample was prepared by a second vacuum distillation. Anal. Found: C, 41.45; H, 2.72%. C$_{14}$H$_{11}$O$_2$Ir Calc.: C, 41.67; H, 2.75%. ^{1}H NMR (CDCl$_3$) δ: 7.37–7.21 (m, 5H, aromatic); 5.45–5.43 (t, 2H, C$_5$H$_4$); 5.38–5.36 (t, 2H, C$_5$H$_4$); 3.76 (s, 2H, CH$_2$) ppm. ^{13}C NMR (CDCl$_3$) δ: 172.95 (CO); 139.50, 128.66, 128.59, 126.81 (C$_6$H$_5$); 107.93, 84.49, 82.34 (C$_5$H$_4$); 34.20 (CH$_2$) ppm. FT-IR (CH$_2$Cl$_2$) (cm^{-1}): 2028.4, 1957.7 (ν_{CO}); (hexane) (cm^{-1}): 2035.0, 1969.3 (ν_{CO}). GC–MS m/e: 402, 404 (M$^+$); 374, 376 (M − CO)$^+$; 346, 348 (M − 2CO)$^+$ (base peak).

3.4. (η^5-Acetylcyclopentadienyl)dicarbonyliridium (13)

Acetylcyclopentadienylsodium [18] (0.73 g, 6.4 mmol) was added to 0.50 g (1.4 mmol) of 4 in 50 ml of benzene and the solution refluxed for 3 d. The reaction was allowed to cool under nitrogen and the solvent removed under vacuum. The residue was extracted with 3 × 20 ml portions of hexane. The hexane fractions were combined, concentrated to ca. 5 ml and placed in a freezer at −15°C for 4 d. The resulting light yellow crystals (0.253 g, 62% yield) were collected and placed under high vacuum to remove all traces of solvent. Anal. Found: C, 30.69; H, 1.90%. C$_9$H$_7$O$_3$Ir Calc.: C, 30.42; H, 1.98%. ^{1}H NMR (CDCl$_3$) δ: 5.83–5.67 (d of t, 4H, C$_5$H$_4$); 2.38 (s, 3H, CH$_3$) ppm. FT-IR (CH$_2$Cl$_2$) (cm^{-1}): 2043.1, 1974.4, 1677.0 (ν_{CO}). ^{13}C NMR (CDCl$_3$) δ: 191.33 (org. CO); 169.86 (inorg. CO); 102.40, 87.99, 82.52 (C$_5$H$_4$); 26.37 (CH$_3$) ppm. GC–MS m/e: 354, 356 (M$^+$); 326, 328 (M − CO)$^+$; 298, 300 (M − 2CO)$^+$ (base peak).

3.5. (η^5-Methylcyclopentadienyl)dicarbonyliridium (5)

Methylcyclopentadiene dimer (20 ml) was added to 50 ml of decalin in a three-necked flask with a Vigreaux column attached. The solution was heated to high temperature and the methylcyclopentadiene monomer was distilled over to a flask containing 40 ml of 1.6 M n-butyllithium and 100 ml of hexane. Solvent was

removed by filtration through a cannula and the white solid was washed with 2×50 ml of hexane.

Methylcyclopentadienyllithium (1.2 g, 13.9 mmol) was then placed in 50 ml of benzene and **4** (0.420 g, 1.16 mmol) added. The solution was refluxed for 2 d and allowed to cool under flowing nitrogen. The benzene was removed under vacuum and the residue extracted with 3×20 ml of hexane. The hexane fractions were combined and the solvent removed. The resulting brown oil was vacuum-distilled ($110°C/0.5$ mmHg) yielding 0.28 g of a golden oil (74% yield). ^1H and ^{13}C NMR spectra as well as GC–MS data indicated the presence of trace amounts of unsubstituted cyclopentadienyldicarbonyliridium. The oil was placed in the freezer and gold crystals were obtained. The crystals were dried under high vacuum to obtain an analytical sample. Anal. Found: C, 29.39; H, 2.15%. $C_8H_7O_2Ir$ Calc.: C, 29.35; H, 2.15%. ^1H NMR (CDCl$_3$) δ: 5.54 (t, 2H, C$_5$H$_4$); 5.32 (t, 2H, C$_5$H$_4$); 2.25 (t, 3H, CH$_3$) ppm. FT-IR (CH$_2$Cl$_2$) (cm^{-1}): 2041.1, 1956.0 (ν_{CO}). ^{13}C NMR (CDCl$_3$) δ: 173.32 (CO); 102.20, 85.48, 82.02 (C$_5$H$_4$); 13.65 (CH$_3$) ppm. GC–MS m/e: 326, 328 (M$^+$); 288, 300 (M – CO)$^+$; 270, 272 (M – 2CO)$^+$ (base peak).

3.6. (η^5-Trimethylsilylcyclopentadienyl)dicarbonyliridium (6)

Trimethylsilylcyclopentadienyllithium [4] (0.502 g, 3.5 mmol) and 0.492 g (1.32 mmol) of **4** were refluxed in 50 ml of freshly distilled benzene for 3 d. The solution was allowed to cool to room temperature, then filtered through a cannula and the solvent removed under high vacuum. The resulting brown residue was microdistilled to give 0.48 g (94% yield) of a bright golden oil. A second microdistillation yielded an analytical sample. Anal. Found: C, 31.43; H, 3.36%. $C_{10}H_{13}O_2SiIr$ Calc.: C, 31.16; H, 3.40%. ^1H NMR (CDCl$_3$) δ: 5.67 (t, 2H, C$_5$H$_4$); 5.40 (t, 2H, C$_5$H$_4$); 0.30 (s, 9H, SiMe$_3$) ppm. ^{13}C NMR (CDCl$_3$) δ: 172.83 (CO); 96.01, 87.41, 86.73 (C$_5$H$_4$); 0.05 (SiMe$_3$) ppm. FT-IR (CH$_2$Cl$_2$) (cm^{-1}): 2029.5, 1958.3 (ν_{CO}); (neat) (cm^{-1}): 2027.6, 1959.0. GC–MS m/e: 386, 384 (M$^+$); 258, 256 (M – CO)$^+$; 330, 328 (M – 2CO)$^+$.

3.7. (η^5-Carbomethoxycyclopentadienyl)dicarbonyliridium (16)

Carbomethoxycyclopentadienylthallium [19] (0.50 g, 1.5 mmol) and 0.30 g (0.83 mmol) of **4** were refluxed in 50 ml of benzene for 4 d. The solution was cooled, filtered through a Florisil–Celite plug and the solvent removed, giving a crude product as a dark brown residue (0.28 g, 84% yield). The residue was extracted with hexane and the extracts placed in a freezer at $-15°C$ overnight yielding yellow crystals, m.p. $35°C$. The crystals (0.07 g) were sublimed to give a bright

yellow solid which showed decomposition in the IR spectrum. Recrystallization of the sublimate in hexane at $-15°C$ gave a small quantity of yellow crystals which after drying under high vacuum were of analytical purity. Anal. Found: C, 28.97; H, 1.69%. $C_9H_7O_4Ir$ Calc.: C, 29.11; H, 1.90%. ^1H NMR (CDCl$_3$) δ: 5.89 (t, 2H, C$_5$H$_4$); 5.64 (t, 2H, C$_5$H$_4$); 3.81 (s, 3H, CH$_3$) ppm. FT-IR (CH$_2$Cl$_2$) (cm^{-1}): 2043.6, 1974.7, 1720.1 (ν_{CO}). GC–MS m/e: 372, 370 (M$^+$); 344, 342 (M – CO)$^+$; 314, 312 (M – CO$_2$Me + H)$^+$; 286, 284 (M – CO$_2$Me – CO + H)$^+$; 258, 256 (M – CO$_2$Me – 2CO + H)$^+$.

3.8. (η^5-Benzoylcyclopentadienyl)dicarbonyliridium (14)

Benzoylcyclopentadienylsodium [20] (0.40 g, 2.1 mmol) and 0.50 g (1.4 mmol) of **4** were refluxed in 50 ml of benzene for 3 d. The solution was allowed to cool to room temperature and filtered through Celite to yield a red–brown solution. After removal of the solvent in a high vacuum, a dark oil remained (0.18 g, 31% yield). The oil was extracted with hexane, giving a yellow solution. Removal of the solvent left a yellow solid (m.p. 74°C) which was crystallized by dissolving it in hot hexane and cooling to $-15°C$ overnight. Sublimation yielded a sample of analytical purity. Anal. Found: C, 40.42; H, 2.17%. $C_{14}H_9O_3Ir$ Calc.: C, 40.28; H, 2.17%. ^1H NMR (CDCl$_3$) δ: 8.00–7.32 (m, 5H, aromatic); 5.85 (t, 2H, C$_5$H$_4$); 5.72 (t, 2H, C$_5$H$_4$) ppm. FT-IR (CH$_2$Cl$_2$) (cm^{-1}); 2043.8, 1976.7, 1645.0 (ν_{CO}). GC–MS m/e: 418, 416 (M$^+$); 390, 388 (M – CO)$^+$; 362, 360 (M – 2CO)$^+$; 77 (C$_6$H$_5$)$^+$; 28 (CO)$^+$.

3.9. (η^5-Cyanocyclopentadienyl)dicarbonyliridium (17)

Cyanocyclopentadienylthallium [4,21] (0.30 g, 1.0 mmol) and 0.20 g (0.55 mmol) of **4** were refluxed in 30 ml of benzene for 3 d. The solution was cooled to room temperature and filtered through Celite to give a red–brown solution. The solvent was removed in a high vacuum to give a dark oil (0.04 g, 18% yield). The oil was passed through a hexane-packed alumina column and a yellow band was isolated by elution with hexane. The solvent was removed leaving only a trace amount of product. ^1H NMR (CDCl$_3$) δ: 5.79 (t, 2H, C$_5$H$_4$); 5.71 (t, 2H, C$_5$H$_4$) ppm. FT-IR (CH$_2$Cl$_2$) (cm^{-1}): 2050.5, 1983.7 (ν_{CO}); 2234.6 (ν_{CN}); (neat) (cm^{-1}): 2055.6, 1985.0 (ν_{CO}); 2228.9 (ν_{CN}). GC–MS m/e: 339, 337 (M$^+$); 311, 309 (M – CO)$^+$; 283, 281 (M – 2CO)$^+$; 257, 255 (M – 2CO – CN)$^+$.

3.10. (η^5-Dimethylaminocyclopentadienyl)dicarbonyliridium (7)

Dimethylaminocyclopentadienyllithium [4,22] (0.75 g, 6.5 mmol) was transferred as a THF solution to a

flask containing 25 ml of THF and 0.54 g (1.7 mmol) of chlorotricarbonyliridium (which had been rigorously dried) at 0°C and the mixture allowed to react for 1 h. The solution darkened but the suspension of chlorotricarbonyliridium was still present. The reaction was then heated at reflux for 2 d and allowed to cool to room temperature. The solvent was removed and the residue extracted with hexane giving a red solution after filtration through Celite. Removal of the hexane gave a dark oil (0.12 g, 23% yield). The oil was microdistilled to give an orange–red oil. TLC indicated a mixture of two compounds (one yellow and one violet). An attempt to chromatograph a small sample on an alumina column was unsuccessful. The oil was then purified on a hexane-packed silica column, eluting with 10% THF and 90% CH_2Cl_2. Removal of the solvent left a yellow oil. ^1H NMR ($CDCl_3$) δ: 5.21 (t, 2H, C_5H_4); 5.08 (t, 2H, C_5H_4); 2.47 (s, 6H, NMe_2) ppm. FT-IR (CH_2Cl_2) (cm^{-1}): 2017.1, 1945.8 (ν_{CO}). GC–MS m/e: 357, 355 (M^+); 329, 327 ($M - CO$)$^+$; 301, 299 ($M - 2CO$)$^+$ (base peak); 285, 283 ($M - NMe_2 - CO$)$^+$.

3.11. (η^5-Chlorocyclopentadienyl)dicarbonyliridium (18)

Chlorocyclopentadienylthallium [11] (0.90 g, 3.0 mmol) and 0.77 g (2.5 mmol) of 4 were refluxed in 50 ml of benzene for 3 d. The solution was allowed to cool to room temperature and the solvent removed. The residue was extracted with hexane and filtered through Celite to give a yellow solution. The solution was concentrated to ca. 5 ml, placed on a hexane-packed alumina column and eluted with hexane to give a single yellow band. The solvent was removed and the residue microdistilled to give 0.65 g of a golden oil (88% yield). ^1H NMR spectroscopy, GC-MS and elemental analysis indicated slight contamination of the product with unsubstituted cyclopentadienyldicarbonyliridium. Anal. Found: C, 25.12; H, 1.29%. $C_7H_4ClO_2Ir$ Calc: C, 24.18; H, 1.16%. ^1H NMR ($CDCl_3$) δ: 5.81 (t, 2H, C_5H_4); 5.34 (t, 2H, C_5H_4) ppm. ^{13}C NMR ($CDCl_3$) δ: 171.56 (CO); 99.44, 85.46, 81.46 (C_5H_4) ppm. FT-IR (neat) (cm^{-1}): 2032, 1961 (ν_{CO}); (CH_2Cl_2) (cm^{-1}): 2039.4, 1969.6. GC–MS m/e: 350, 348, 346 (M^+); 322, 320, 318 ($M - CO$)$^+$; 294, 292, 290 ($M - 2CO$)$^+$ (base peak).

3.12. (η^5-Pentabenzylcyclopentadienyl)dicarbonyliridium (8)

Pentabenzylcyclopentadiene [23] (1.002 g, 1.94 mmol) was reacted with 1.5 ml of 1.6 M ^nBuLi in 50 ml of benzene, producing a deep red solution after 2 h. A benzene solution (20 ml) containing 0.703 g (1.94 mmol) of 4 was added slowly and the mixture was refluxed for 3 d. The reaction mixture was allowed to

cool and 2.0 g of alumina was added. The benzene was removed and the residue was added to a dry packed alumina column. Elution with 1 : 3 benzene/pentane gave a single yellow band. Concentration to ca. 10 ml and storage in a freezer produced a mixture of yellow (0.12 g) and white crystals (0.48 g) which were mechanically separated. FT-IR spectroscopy indicated that the yellow crystals were the desired product (8.2% yield). Repeated recrystallizations from hexane yielded cubic yellow crystals that melted at 97.5°C. Anal. Found: C, 65.88; H, 4.65%. $C_{41}H_{35}O_2Ir$ Calc.: C, 66.03; H, 4.62%. ^1H NMR ($CDCl_3$) δ: 7.14–6.97 (m, 25H, C_6H_5); 3.69 (s, 10H, CH_2) ppm. ^{13}C NMR ($CDCl_3$) δ: 175.02 (CO); 139.77, 128.54, 128.16, 126.31 (C_6H_5); 102.93 (C_5); 30.98 (CH_2) ppm. FT-IR (CH_2Cl_2) (cm^{-1}): 2018.1, 1948.7 (ν_{CO}). MS m/e: 764, 762 (M^+); 736, 734 ($M - CO$)$^+$.

3.13. (η^5-Tetraphenylcyclopentadienyl)dicarbonyliridium (9)

Tetraphenylcyclopentadiene [24] (0.95 g, 2.56 mmol) was treated with 1.6 ml of 1.6 M ^nBuLi in 50 ml of THF for 4 h, resulting in a red solution that fluoresced blue–green. A 25 ml solution of THF with 0.602 g (1.66 mmol) of 4 was transferred by cannula to the reaction flask and the mixture refluxed for 2 d. After cooling to room temperature, the solvent was removed and the residue extracted with 2 × 75 ml of hexane which was filtered through a cannula. The hexane fractions were combined, concentrated to ca. 20 ml and placed in a freezer for 4 d. Brown crystal clusters of 9 (0.36 g, 35% yield) were obtained. Repeated crystallizations from hexane resulted in cubic yellow crystals, m.p. 148–150°C. Anal. Found: C, 61.04; H, 3.60%. $C_{31}H_{21}O_2Ir$ Calc.: C, 60.28; H, 3.43%. ^1H NMR indicated continued contamination by a trace amount of tetraphenylcyclopentadiene. ^1H NMR ($CDCl_3$) δ: 7.32–6.95 (m, 20H, C_6H_5); (6.07, 1H, C_5H) ppm. ^{13}C NMR ($CDCl_3$) δ: 173.43 (CO); 132.82, 132.07, 131.02, 130.06, 129.85, 128.18, 127.93, 127.73, 127.61 (C_6H_5)$_4$; 107.91, 106.09, 81.85 (C_5H) ppm. FT-IR (CH_2Cl_2) (cm^{-1}): 2027.2, 1959.9 (ν_{CO}). MS m/e: 618, 616 (M^+); 590, 588 ($M - CO$)$^+$; 562, 560 ($M - 2CO$)$^+$.

3.14. (η^5-2-Methoxyethylcyclopentadienyl)dicarbonyliridium (12)

2-Methoxyethylcyclopentadiene [25] (0.41 g, 3.30 mmol) was reacted with 2.1 ml of 1.6 M n-butyllithium in THF and stirred for 4 h. A THF solution of 0.502 g (1.38 mmol) of 4 was added by cannula at −78°C and allowed to warm to room temperature. The solution was stirred at room temperature overnight and the solvent was then removed under vacuum. The crude material

was microdistilled and the resulting yellow oil (0.145 g, 26.5% yield) analyzed by ^{1}H NMR and FT-IR spectroscopy and by GC-MS methods. ^{1}H NMR (CDCl$_3$) δ: 5.51 (t, 2H, C$_5$H$_4$); 5.37 (t, 2H, C$_5$H$_4$); 3.51 (t, 2H, CH$_2$); 3.35 (s, 3H, OCH$_3$); 2.61 (t, 2H, CH$_2$) ppm. ^{13}C NMR (CDCl$_3$) δ: 173.16 (CO); 106.17, 84.62, 82.04 (C$_5$H$_4$); 75.11 (CH$_2$); 58.63 (CH$_2$); 27.70 (CH$_3$) ppm. FT-IR (CH$_2$Cl$_2$) (cm^{-1}): 2027.9, 1956.6 (ν_{CO}). GC–MS m/e: 372, 370 (M$^+$); 344, 342 (M − CO)$^+$; 316, 314 (M − 2CO)$^+$; 312, 310 (M − C$_2$H$_4$OCH$_3$)$^+$ (base peak).

3.15. (η^5-2-Dimethylaminoethylcyclopentadienyl)dicarbonyliridium (10)

2-Dimethylaminoethylcyclopentadiene [26] (1.7 g, 17 mmol) was reacted with 10.75 ml of 1.6 M n-butyllithium in 90 ml of hexane and stirred overnight. A 10 ml solution of 0.90 g (2.48 mmol) of **4** in hexane was transferred to the reaction flask by cannula and the mixture refluxed for 3 d. The solution was allowed to cool and then filtered by cannula, the solvent removed and the residue was vacuum-distilled at ca. 90°C/5 mmHg. A golden yellow oil was obtained (0.42 g, 1.09 mmol, 44.7% yield). Repeated vacuum distillation yielded a sample of analytical purity. Anal. Found: C, 34.06; H, 3.68; N, 3.64%. C$_{11}$H$_{14}$NO$_2$Ir Calc.: C, 34.37; H, 3.67; N, 3.64%. ^{1}H (CDCl$_3$) δ: 5.52 (m, 2H, C$_5$H$_4$); 5.37 (m, 2H, C$_5$H$_4$); 2.58–2.36 (m, 4H, CH$_2$CH$_2$); 2.26 (t, 6H, NCH$_3$) ppm. ^{13}C (CDCl$_3$) δ: 173.20 (CO); 106.83, 84.45, 81.97 (C$_5$H$_4$); 62.67 (CH$_2$); 45.44 (CH$_3$); 25.71 (CH$_2$) ppm. FT-IR (CH$_2$Cl$_2$) (cm^{-1}): 2023.5, 1957.0 (ν_{CO}). MS m/e: 385, 383 (M$^+$); 357, 355 (M − CO)$^+$ (base peak); 329, 327 (M − 2CO)$^+$.

3.16. [η^5-(2-Dimethylaminoethyl)(tetramethyl)cyclopentadienyl]dicarbonyliridium (11)

2-Dimethylaminoethyl(tetramethyl)cyclopentadiene [27] (1.26 g, 6.52 mmol) was treated with 4.07 ml of 1.6 M n-butyllithium in 50 ml of THF to give a yellow solution. A THF solution of 0.702 g (1.91 mmol) of **4** was added by cannula and the mixture refluxed for 3 d. The solution was allowed to cool and was filtered by cannula. The solvent was removed and the residue was vacuum-distilled (150°C/0.5 mmHg) to give 0.68 g (92% crude yield) of an orange oil. NMR and FT-IR spectroscopy indicated substantial contamination with free ligand. The oil was chromatographed on a 14 cm wet-packed basic-washed alumina column and eluted with methylene chloride to give a single yellow band. The solvent was removed and the yellow oil was vacuum-distilled (150°C/0.5 mmHg) to give a golden oil which crystallized in a freezer at −15°C. The resulting crystalline solid melted sharply in the range 39–40°C.

The solid was placed under high vacuum overnight and submitted for elemental analysis. Anal. Found: C, 41.53; H, 5.15; N, 3.11%. C$_{15}$H$_{22}$NO$_2$Ir Calc.: C, 40.89; H, 5.03; N, 3.18%. ^{1}H NMR (CDCl$_3$) δ: 2.63–2.55 (m, 2H, CH$_2$); 2.33–2.25 (m + s, 8H, CH$_2$, NCH$_3$); 2.19, 2.18 [2 s, 12H, (CH$_3$)$_4$] ppm. ^{13}C NMR (CDCl$_3$) δ: 176.68 (CO); 100.55, 97.84, 96.81 (C$_5$); 62.71 (NCH$_2$); 45.42 [N(CH$_3$)$_2$]; 23.21 (CH$_2$); 10.70, 10.53 [(CH$_3$)$_4$] ppm. FT-IR (CH$_2$Cl$_2$) (cm^{-1}): 2009.5, 1938.1 (ν_{CO}). MS m/e: 441, 439 (M$^+$); 413, 411 (M − CO)$^+$ (base peak); 385, 383 (M − 2CO)$^+$.

3.17. (η^5-Pentamethylcyclopentadienyl)dicarbonyliridium (3) [2]

Pentamethylcyclopentadienyllithium (1.22 g, 8.58 mmol) was reacted with 1.83 g (4.98 mmol) of **4** in 50 ml of benzene. The solution was refluxed for 3 d, allowed to cool to room temperature and the solvent removed. The solid residue was transferred to a sublimer and heated to 95°C at 0.2 mmHg overnight to give 1.61 g (84% yield) of yellow crystals. ^{1}H NMR (CDCl$_3$) δ: 2.19 (s, 15H, CH$_3$) ppm. ^{13}C NMR (CDCl$_3$) δ: 176.95 (CO); 97.43 (C$_5$); 10.65 (CH$_3$) ppm. FT-IR (CH$_2$Cl$_2$) (cm^{-1}): 2009.8, 1939.2 (ν_{CO}). MS m/e: 384, 382 (M$^+$); 356, 354 (M − CO)$^+$; 328, 326 (M − 2CO)$^+$.

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