Synthesis and Hammett Constant Correlation Studies of New Functionally Substituted (η^5-Cyclopentadienyl)carbonyl(triphenylphosphine)iridium Compounds

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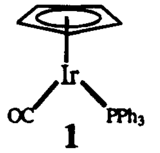
A series of functionally substituted (η^5-cyclopentadienyl)carbonyl(triphenylphosphine)iridium compounds of the type Ir(η^5-C_5H_4R)(CO)(PPh_3) (R = C(O)CH_3, CH_3, C(O)C_6H_5, CHO, $SiMe_3$, NMe_2, CO_2CH_3, $CH_2C_6H_5$, CN, Cl) have been prepared from reactions of the corresponding substituted cyclopentadienylthallium, -sodium, or -lithium reagents with *trans*-chlorocarbonylbis(triphenylphosphine)iridium, or by reaction of these intermediates with chlorotricarbonyliridium and subsequent reaction with triphenylphosphine. The carbonyl stretching frequencies and the ^{31}P NMR chemical shifts of these compounds have been correlated with various Hammett substituent constants. Greatest linearity was achieved with parameters that represent the sum of the inductive and resonance effects of the substituents.

Introduction

Recent studies in our laboratory and elsewhere have described the synthesis and characterization of a series of ring-substituted (η^5-cyclopentadienyl)dicarbonylrhodium compounds.[1-3] Correlations have been studied between Hammett-type substituent constants for the various ring substituents versus reaction kinetics, carbonyl stretching frequencies, and ^{103}Rh NMR chemical shifts.[1-3] In contrast, functionally substituted (η^5-cyclopentadienyl)iridium compounds are virtually unknown, except for Ir(η^5-$C_5H_4CH{=}CH_2$)$(CO)_2$,[4,5] [Ir(η^5-C_5H_4)PR_2(CO)]$_2$ (R = Ph, Me),[6,7] and Ir(η^5-$C_5H_4PPh_2$)(CO)(PPh_3).[7]

We report here on synthetic studies leading to a wide variety of new functionally substituted derivatives of (η^5-cyclopentadienyl)carbonyl(triphenylphosphine)iridium (**1**), and we examine correlations of the carbonyl stretching frequencies and the ^{31}P NMR chemical shifts of these compounds with the various Hammett constants for the substituents on the η^5-cyclopentadienyl ring.



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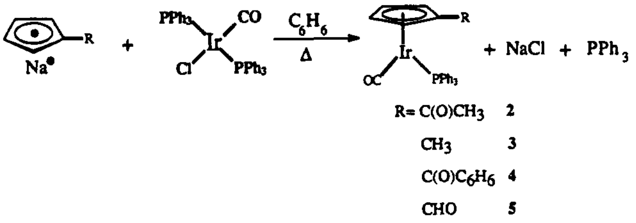
Results and Discussion

Synthetic Studies. Sodium salts of substituted cyclopentadienyl ligands proved to be highly reactive with *trans*-chlorocarbonylbis(triphenylphosphine)iridium (Vaska's Compound), giving excellent yields of products in nearly all cases. Scheme 1 shows the compounds prepared by this method. (η^5-Acetylcyclopentadienyl)carbonyl(triphenylphosphine)iridium (**2**) was obtained in 59% yield as an orange crystalline solid. The compound was air-stable and showed no change in its proton NMR spectrum after one year. (η^5-Methylcyclopentadienyl)carbonyl(triphenylphosphine)iridium (**3**) was also prepared in excellent yield (79%) by this method. It was isolated as dark orange crystals that were relatively air-stable (they discolor in air overnight but no change in the proton NMR spectrum was noted). (η^5-Benzoylcyclopentadienyl)carbonyl(triphenylphosphine)iridium (**4**) was isolated as a yellow powdery solid that resisted all attempts at crystallization, and the yield was low for the purified product (30%). Much of the product was lost in the purification process, resulting in the low yield. (η^5-Formylcyclopentadienyl)carbonyl(triphenylphosphine)iridium (**5**) could not be obtained in either crystalline form or analytical purity. The compound tended to decompose during crystallization and chromatography. The crude yellow powder was analyzed spectroscopically, however, and its proton NMR and FTIR spectra were consistent with the proposed structure.

Scheme 1



The lithium salts of substituted cyclopentadienyl ligands shown in Scheme 2 also proved useful in the reactions with *trans*-chlorocarbonylbis(triphenylphosphine)iridium. The ease of preparation of [(trimethylsilyl)cyclopentadienyl]lithium makes it an extremely

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[1] Cheong, M.; Basolo, F. *Organometallics* **1988,** *7,* 2041.

[2] Graham, P. B.; Rausch, M. D.; Taschler, K.; von Philipsborn, W. *Organometallics* **1991,** *10,* 3049.

[3] Koller, M.; von Philipsborn, W. *Organometallics* **1992,** *11,* 467.

[4] Macomber, D. W.; Hart, W. P.; Rausch, M. D.; Priester, R. D.; Pittman, C. U., Jr. *J. Am. Chem. Soc.* **1982,** *104,* 884.

[5] Macomber, D. W.; Spink, W. C.; Rausch, M. D. *J. Organomet. Chem.* **1983,** *250,* 311.

[6] Rausch, M. D.; Spink, W. C.; Atwood, J. L.; Baskar, A. J.; Bott, S. G. *Organometallics* **1989,** *8,* 2627.

[7] Xiadong, H.; Maisonnat, A.; Duhan, F.; Poilblanc, R. *Organometallics* **1987,** *6,* 678.

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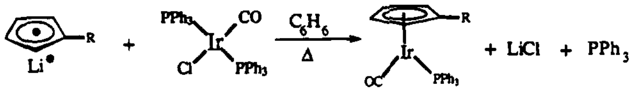
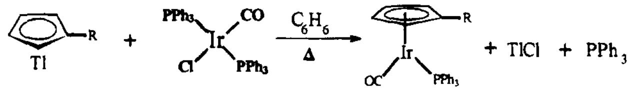
Scheme 2



R = SiMe3 **6**
NMe2 **7**

Scheme 3



R= CO2Me **8**
CH2C6H5 **9**
CN **10**

attractive ligand for organometallic synthesis. [η^5-(Trimethylsilyl)cyclopentadienyl]carbonyl(triphenylphosphine)iridium (**6**) was obtained in high yield (69%) as orange cubic crystals. The crystals were stable in air for extended periods showing no change in color or proton NMR spectrum. [η^5-(Dimethylamino)cyclopentadienyl]carbonyl(triphenylphosphine)iridium (**7**) could not be isolated as an analytically pure sample. It was very air- and moisture-sensitive. The proton NMR, ^{31}P NMR, and FTIR spectra obtained for the crude product, however, were consistent with the proposed structure. The synthesis of **7** by this method was verified by its preparation from a reaction between the related dicarbonyl compound, $Ir(\eta^5\text{-}C_5H_4NMe_2)(CO)_2$, prepared in a separate study, and triphenylphosphine. Identical spectral data were obtained by both routes.

The organoiridium compounds shown in Scheme 3 were prepared from the corresponding substituted cyclopentadienylthallium intermediates. The organothallium compounds had the advantage of being generally more stable than the corresponding lithium and sodium derivatives. This feature was very important in the reactions involving Vaska's compound because of the required reaction conditions.

(η^5-Carbomethoxycyclopentadienyl)carbonyl(triphenylphosphine)iridium (**8**) was prepared in good yield (60%) by means of the corresponding cyclopentadienylthallium compound. The orange crystals obtained were relatively air-stable, becoming darker on exposure to air overnight but showing no change in the proton NMR spectrum. (η^5-Benzylcyclopentadienyl)carbonyl(triphenylphosphine)iridium (**9**) was prepared in good yield (54%) from the corresponding cyclopentadienylthallium compound. Compound **9** resisted all attempts at crystallization but an analytically pure sample was obtained as a waxy red-brown solid. The compound was air stable and survived extended handling in nondried solvents. (η^5-Cyanocyclopentadienyl)carbonyl(triphenylphosphine)iridium (**10**) was prepared from the corresponding thallium compound, but was not obtained in analytical purity due to the extremely low yield. However, (η^5-cyanocyclopentadienyl)carbonyl(triphenylphosphine)iridium (**10**) gave excellent IR and proton NMR spectroscopic data.

(η^5-Chlorocyclopentadienyl)carbonyl(triphenylphosphine)iridium (**12**) was prepared via a two-step process using (η^5-chlorocyclopentadienyl)dicarbonyliridium (**11**) as shown in Scheme 4. The product was obtained in 20% yield as an air-stable, yellow, crystalline solid. All attempts to synthesize **12** directly from *tran*-chlorocarbonylbis(triphenylphosphine)iridium and chlorocyclopentadienylthallium resulted in decomposition.

Scheme 4

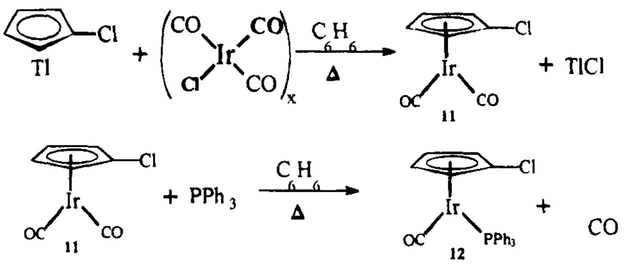


Table 1. IR and ^{31}P NMR Data for the Functionality Substituted (η^5-Cyclopentadienyl)carbonyl(triphenylphosphine)iridium Compounds

compd no.	ligand	ν_{CO}, cm^{-1} [a]	^{31}P chem shift in ppm[a]
1	H	1924.0	16.31
2	COMe	1941.6	14.42
3	CH_3	1922.1	16.96
4	COPh	1942.1	14.26
5	CHO	1945.9	13.71
6	$SiMe_3$	1923.0	16.46
7	NMe_2	1911.7	16.07
8	CO_2Me	1942.5	14.55
9	CH_2Ph	1924.4	16.56
10	CN	1953.8	13.75
12	Cl	1934.3	15.91
13[b]	PPh_2	1928.0	16.08

[a] Recorded in CH_2Cl_2 solution. [b] Data obtained from literature (ref 7).

Substituted cyclopentadienyllithium, -sodium, and -thallium compounds therefore generally yield good to excellent results when reacted with *trans*-chlorocarbonylbis(triphenylphosphine)iridium in benzene at reflux for several days. In several cases where the substituted cyclopentadienyl–metal reagent is not thermally stable under these conditions [i.e. $(C_5H_4CF_3)Tl$[8]], unsatisfactory results were obtained. As a general route to this class of compounds, *trans*-chlorocarbonylbis(triphenylphosphine)iridium gives excellent results at reasonable cost.

Substituted (η^5-cyclopentadienyl)carbonyl(triphenylphosphine)iridium compounds generally exhibit an AA'BB' splitting pattern (pseudo triplets) in their ^1H NMR spectra, if the substituent cannot spin couple with the ring protons. Where coupling occurs, the ring protons in the A and A' positions appear as an unresolved multiplet. Most of the new organoiridium compounds have been characterized by satisfactory elemental analyses and mass spectra as well as by their IR and ^{31}P NMR spectra which are discussed below.

Correlation of Spectral Data with Substituent Constants. Relevant IR and ^{31}P NMR spectral data for functionally substituted derivatives of **1** are summarized in Table 1. The data points in Table 1 were obtained using the same solvent, concentration, temperature, and the same spectrometers to ensure that no determinate errors of measurement interfere with the correlations. The graphing and line fitting for the correlations were performed using DeltaGraph Professional for Windows, a software product of DeltaPoint Inc., on an IBM compatible 80486 computer processor. Correlation coefficients are included with each graph.

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[8] Gassman, P. G.; Winter, C. H. *J. Am. Chem. Soc.* **1986**, *108*, 4228.

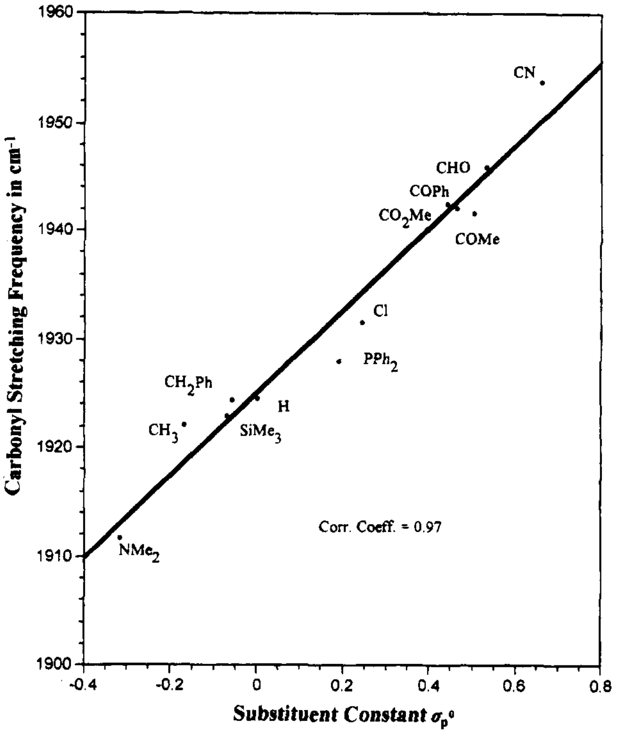

Figure 1. Correlation of carbonyl stretching frequency data with $\sigma_p{}^0$.

Table 2. Correlation of Substituent Parameters with IR and ^{31}P NMR Spectral Data

substituent constant	correl coeff vs freq ν_{CO}	correl coeff vs ^{31}P NMR chem shift	correl coeff vs ^{31}P NMR chem shift (excluding NMe_2)
σ_m	0.90	0.81	0.84
σ_p	0.90	0.61	0.94
σ_{p^0}	0.97	0.83	0.94
σ_{p+}	0.78	0.44	0.94
σ_{p-}	0.93	0.85	0.92
F	0.69		0.57
R	0.70		0.69

Table 2 lists the specific substituent constants[9] and the corresponding correlation coefficients for each of the plots from the correlations obtained from the functionally substituted (η^5-cyclopentadienyl)carbonyl(triphenylphosphine)iridium compounds. Examination of the correlation coefficients in the carbonyl stretching frequency series shows that the greatest linearity was obtained for the constant which measures the substituent effect separated from the aromatic ring by a methylene group, σ_{p^0} (Figure 1). Such a result indicates that the sum of the inductive and resonance effects of the substituent has the greatest impact on the bond order of the terminal carbonyl. This is a logical conclusion, since the effect observed represents the ability of the iridium to back-donate electron density into the unfilled π^* molecular orbital of the terminal carbonyl. Both types of electronic effects will influence the electron density on the metal.

The Hammett constant σ_{p-}, which reflects the substituent effect on a reaction on the aromatic ring resulting in an increase in negative charge in the transition state, exhibited an unexpectedly large correlation with the carbonyl stretching frequency. This result is also logical if one considers the anionic nature of the cyclopentadienyl ring. Electron-donating groups on the cyclopentadienyl ring increase the net negative charge on the ring which then can shift some of that increase in charge to the iridium atom. The excess electronic charge placed on the metal is then available for donation to the π^* orbital of the terminal carbonyl. The anionic nature of the cyclopentadienyl ligand also can account for the low correlation with the constant σ_{p+}.

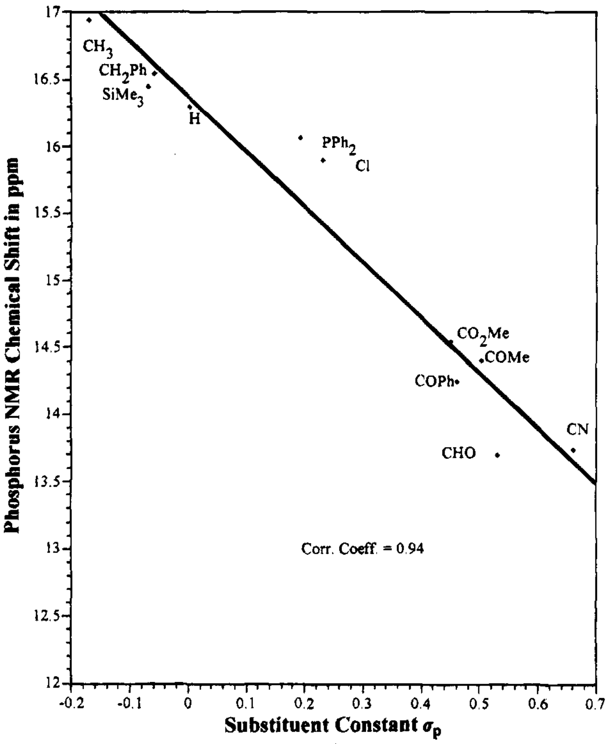

Figure 2. Correlation of ^{31}P NMR chemical shift with σ_p (data point for **7** not included).

The poor correlations obtained for the Taft field and resonance constants, F and R, indicate that a combination of both resonance and inductive effects influence the carbonyl stretching frequency. All of the effects noted for the carbonyl series correlations were in accord with previous studies done on rhodium and chromium compounds.[2,3,10]

Two questions needed to be addressed in the ^{31}P NMR chemical shift correlations. Why is a negative slope obtained in all the correlations, and why is [η^5-(dimethylamino)cyclopentadienyl]carbonyl(triphenylphosphine)iridium (**7**) so different in behavior from all the other compounds synthesized for this section?

Discounting **7** for the moment, all of the variants of the σ_p constant give highly linear correlations, as illustrated by Figure 2, but they all have negative slopes which is the opposite of what is expected. This same phenomenon was also reported but not explained in Bitterwolf's study on substituted arene–chromium systems.[10] A negative slope to the Hammett plot implies that the more electron-withdrawing substituents result in a more shielded phosphorus. Such a result is exactly the opposite of what would be predicted based on the findings in the carbonyl series of correlations. If we

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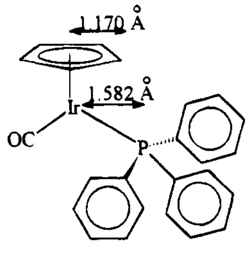
[9] A number of excellent compendia of Hammett and related substituent constants that contain all of the substituents included in this study are available: (a) Hansch, C.; Taft, R. W. I. *Chem. Rev.* **1991**, *91*, 165. (b) Hansch, C.; Leo, A.; Unger, S. H.; Kim, K. W.; Nikaitani, D.; Lein, E. J. *J. Med. Chem.* **1973**, *16*, 1207.

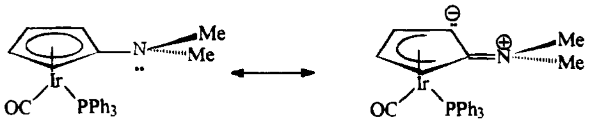
[10] Bitterwolf, T. E. *Polyhedron* **1988**, *15*, 1377.

restate the phenomenon as a less deshielded phosphorus, then we could relate the electron-withdrawing ligands to an event which decreases a deshielding effect on the phosphorus nucleus.

A possible answer can be extrapolated from the X-ray structure of the parent compound, **1**.[11] The phosphorus atom in the molecular structure of **1** is outside of the cylinder created by the projection of the cyclopentadienyl ring by 0.0412 Å. The anisotropic magnetic field created by the aromatic ring current of the cyclopentadienyl ring in a bulk magnetic field is weakly deshielding in the region where the phosphorus is located. The substituents affect the π-electron density of the cyclopentadienyl ring. Electron-withdrawing substituents could be expected to decrease the electron density on the ring and therefore decrease the intensity of the anisotropic effect. This factor could give rise to the observed phenomena of an electron-withdrawing group causing greater shielding of the phosphorus nucleus. Such a process requires that the anisotropic effect be of greater magnitude than the inductive shielding and deshielding effects. The net change in chemical shift from the most shielded to the least shielded substituted (η^5-cyclopentadienyl)carbonyl(triphenylphosphine)iridium compound is only 3.29 ppm. This is a very small range for phosphorus chemical shifts and is a reasonable range for the expected variance due to this effect.



The other question to answer is why does the ^{31}P NMR chemical shift for **7** vary so far from the expected value? A possible answer comes from the work of Boche et al. on the (dimethylamino)cyclopentadienyl ligand and their preparation of the substituted metallocenes.[12] They noted that the C−N bond distance in bis-(dimethylamino)titanocene dichloride was considerably shorter than normal based on X-ray crystal structure data. This finding indicates that there is significant double bond character present. If this fact also applies to [η^5-(dimethylamino)cyclopentadienyl]carbonyl(triphenylphosphine)iridium (**7**) then the nonaromatic structure illustrated below



could be a major contributing resonance form. This type of resonance structure was proposed by Basolo et al. to account for the deviation in rates of ligand substitution seen for cyclopentadienyl ligands with hetero atoms in the α position having lone pairs of electrons.[1] The significant reduction of the aromatic character of the cyclopentadienyl ring for **7** should also significantly reduce the anisotropic effect felt by the phosphorus nucleus. Therefore, the inductive effect could become the dominant factor determining the chemical shift of the phosphorus. Such a process could therefore account for the anomalous behavior of the dimethylamino-substituted derivative **7** in the phosphorus NMR spectrum. The low carbonyl stretching frequency expected and found for this compound is consistent with the nonaromatic resonance illustrated. The greater electron density transferred to the metal increases its ability to back-donate to the terminal carbonyl ligand.

Experimental Section

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 FTIR or a Perkin-Elmer 1310 infrared spectrometer. Solid samples were prepared as CH_2Cl_2 solutions using subtraction techniques to remove solvent signals and liquid samples were prepared as thin films on NaCl plates. Proton and ^{31}P NMR spectra were recorded on IBM NR-80 or Varian 300 MHz spectrometers. GCMS were recorded on a HP 5970A gas chromatograph−mass spectrometer, using an HP-5 column, 2 min delay time, and 1200 eV ionization energy. Solid sample mass spectra were performed at the University of Berlin on a Varian MAT 311 mass spectrometer using a 70 eV ionization energy. *trans*-Chlorocarbonylbis(triphenylphosphine)iridium was prepared by a literature method.[13] Chlorotricarbonyliridium was purchased from Strem Chemicals. Cyclopentadienyllithium was prepared by reacting equimolar amounts of freshly cracked cyclopentadiene and *n*-butyllithium in tetrahydrofuran (THF) or diethyl ether. Cyclopentadienylsodium was prepared by reacting excess freshly cracked cyclopentadiene with metallic sodium pellets or dispersion in THF. After removing the THF in vacuum and triturating with hexane, the white solid was collected and kept under N_2 until further use. Cyclopentadienylthallium was prepared by reaction of freshly cracked cyclopentadiene with either TlCl or Tl_2SO_4 and KOH in aqueous solution using the high setting of a blender to vigorously agitate the solution.[14] Benzene, hexane, pentane, and toluene were dried over NaK alloy and distilled under argon. THF and diethyl ether were predried over Na wire, and both were dried over NaK alloy and distilled under argon. Melting points are uncorrected and were determined under nitrogen atmosphere in sealed capillary tubes. All elemental analysis were performed by the Microanalytical Laboratory, University of Massachusetts.

(η^5-Cyclopentadienyl)carbonyl(triphenylphosphine)iridium.[15] Cyclopentadienylsodium (0.20 g, 2.3 mmol) and *trans*-chlorocarbonylbis(triphenylphosphine)iridium (0.50 g, 0.64 mmol) were refluxed in 25 mL of toluene overnight. The resulting red-brown solution was passed through a Florisil−Celite plug and concentrated to ca. 5 mL of toluene, and 20 mL of hexane was added. The solution was placed in the freezer at −15 °C for 1 week. Bright orange crystals (0.27 g, 60% yield) were collected. ^{1}H NMR ($CDCl_3$): δ 5.12 (s, 5 H, C_5H_5), 7.20−7.70 (m, 15 H, aromatic). FTIR: ν_{CO} 1944 (cyclohexane), 1924.6 cm^{-1} (CH_2Cl_2). ^{31}P NMR (CH_2Cl_2): δ 16.31 (s).

(η^5-Acetylcyclopentadienyl)carbonyl(triphenylphosphine)iridium (2). *trans*-Chlorocarbonylbis(triphenylphosphine)iridium (0.71 g, 0.91 mmol) and (acetylcyclopentadienyl)sodium (0.50 g, 3.8 mmol)[16] were refluxed in 50 mL

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[11] Bennett, M. S.; Pratt, J. L.; Tuggle, R. M. *Inorg. Chem.* **1974**, *13*, 2408.

[12] Stahl, K. P.; Boche, G.; Massa, W. *J. Organomet. Chem.* **1984**, *277*, 113.

[13] Klabunde, U. *Inorg. Synth.* **1974**, *15*, 82.

[14] Hunt, C. C.; Doyle, J. R. *Inorg. Nucl. Chem. Let.* **1966**, *2*, 283.

[15] Oliver, A. J.; Graham, W. A. G. *Inorg. Chem.* **1970**, *9*, 2653.

of benzene for 4 days. The brown solution was passed through a Florisil−Celite plug and concentrated to ca. 5 mL, 25 mL of hexane was added, and the solution was placed in the freezer at −15 °C for 6 days. Orange crystals (0.32 g) were collected (59% yield). The crystals were dissolved in a minimum of CH_2Cl_2, and hexane was added until the solution started to turn cloudy and then placed in the freezer at −15 °C for 10 days. The resulting orange crystals were dried at 70 °C for 3 days (mp 143 °C). Anal. Calcd for $C_{26}H_{22}O_2PIr$: C, 52.96; H, 3.76. Found: C, 53.07; H, 3.78. ^1H NMR ($CDCl_3$): δ 7.70−7.25 (m, 15 H, aromatic), 5.44 (t, 2 H, C_5H_4), 5.12 (t, 2 H, C_5H_4), 2.15 (s, 3 H, CH_3). FTIR (CH_2Cl_2): ν_{co} 1941.6, 1651.9 cm^{-1}. MS: *m/e* 590, 588 (M^+); 562, 560 $(M - CO)^+$; 519, 517 $(M - CO - COCH_3)^+$; 108 $(C_5H_4COCH_3)^+$; 262 $(PPh_3)^+$; 28 $(CO)^+$. ^{31}P NMR (CH_2Cl_2): δ 14.42 (s).

(η^5-Carbomethoxycyclopentadienyl)carbonyl(triphenylphosphine)iridium (8). (Carbomethoxycyclopentadienyl)thallium[17] (0.50 g, 1.5 mmol) and *trans*-chlorocarbonylbis(triphenylphosphine)iridium (0.75 g, 0.96 mmol) were refluxed in 50 mL of benzene for 4 days. The brown solution was passed through a Florisil−Celite plug, giving a bright golden solution which was concentrated to ca. 5 mL. Hexane (20 mL) was added and the solution placed in the freezer at −15 °C. The orange-yellow crystals (0.35 g, 60% yield) obtained were dissolved in a minimum of CH_2Cl_2, and hexane was added until the solution began to cloud and then placed in a −50 °C bath for 2 weeks, resulting in orange crystals (mp 111 °C). Anal. Calcd for $C_{26}H_{22}O_3PIr$: C, 51.56; H, 3.66. Found: C, 51.42; H, 3.61. ^1H NMR ($CDCl_3$): δ 7.70−7.35 (m, 15 H, aromatic), 5.38 (m, 2 H, C_5H_4), 5.26 (m, 2 H, C_5H_4), 3.64 (s, 3 H, CH_3). FTIR (CH_2Cl_2): ν_{co} 1942.5, 1729.0 cm^{-1}. ^{31}P NMR (CH_2Cl_2): δ 14.55 (s).

(η^5-Benzylcyclopentadienyl)carbonyl(triphenylphosphine)iridium (9). (Benzylcyclopentadienyl)thallium[18] (0.60 g, 1.7 mmol) and *trans*-chlorocarbonylbis(triphenylphosphine)iridium (0.90 g, 1.2 mmol) were refluxed in 50 mL of benzene for 4 days. The dark brown solution was passed through a Florisil−Celite plug giving a red-brown solution. Attempted crystallizations failed in a variety of solvents and mixed solvent systems. Removal of all the solvent yielded a brown sticky solid (0.41 g, 54% yield) which was repeatedly washed with pentane. After careful review of the NMR and IR spectra, the sample was sent for elemental analysis as a waxy red-brown solid. Anal. Calcd $C_{31}H_{26}OPIr$: C, 58.39; H, 4.11. Found: C, 58.51; H, 4.36. ^1H NMR ($CDCl_3$): δ 7.68−7.20 (m, 20 H, aromatic), 5.07 (m, 2 H, C_5H_4), 4.82 (t, 2 H, C_5H_4), 3.58 (s, 2 H, CH_2). FTIR (CH_2Cl_2): ν_{co} 1924.4 cm^{-1}. MS: *m/e* 638, 636 (M^+); 610, 608 $(M - CO)^+$; 262 $(PPh_3)^+$; 155 $(C_5H_4CH_2C_6H_5)^+$. ^{31}P NMR (CH_2Cl_2): δ 16.56 (s).

(η^5-Methylcyclopentadienyl)carbonyl(triphenylphosphine)iridium (3). Methylcyclopentadiene dimer was thermally cracked in decahydronaphthalene and distilled over as the monomer into a suspension of sodium metal sand and THF which reacted to give methylcyclopentadienyl sodium. The solvent was removed under vacuum and the solid triturated with pentane. The solid was collected on a Schlenk filter, washed with 20 mL of pentane, and dried under vacuum. This salt is highly pyrophoric on exposure to air. *trans*-Chlorocarbonylbis(triphenylphosphine)iridium (0.7 g, 0.9 mmol) and (methylcyclopentadienyl)sodium (1.0 g, 9.8 mmol) were refluxed in 50 mL of benzene for 5 days and then filtered through a Florisil−Celite plug to give a golden yellow solution. The solution was concentrated to ca. 5 mL, 20 mL of hexane was added, and then it was placed in the freezer at −15 °C for 4 days. A mixture of orange and yellow crystals (0.40 g, 79% yield) was obtained. The crystals were separated by hand using forceps and a magnifying glass. An NMR spectrum indicated that the orange crystals were the desired product (mp 114 °C). The yellow crystals were starting material, *trans*-chlorocarbonylbis(triphenylphosphine)iridium. The orange crystals were recrystallized by dissolving them in a minimum of CH_2Cl_2 and adding hexane until the solution started to become cloudy. The solution was placed in a −50 °C bath for 1 week and orange crystals were obtained. Anal. Calcd for $C_{25}H_{22}OPIr$: C, 53.46; H, 3.95. Found: C, 53.35; H, 4.06. ^1H NMR ($CDCl_3$): δ 7.80−7.15 (m, 15 H, aromatic), 5.22 (m, 2 H, C_5H_4), 4.83 (m, 2 H, C_5H_4), 2.00 (s, 3 H, CH_3). FTIR (CH_2Cl_2): ν_{co} 1922.1, aromatic C−H stretch 3054.0 cm^{-1}, aliphatic C−H stretch 2986.2 cm^{-1}. MS: *m/e* 562, 560 (M^+); 547, 545 $(M - CH_3)^+$; 534, 532 $(M - CO)^+$; 455, 453 $(M - CO - C_5H_4CH_3)^+$; 262 $(PPh_3)^+$; 78 $(C_5H_4CH_2)^+$; 28 $(CO)^+$. ^{31}P NMR (CH_2Cl_2): δ 16.96 (s).

(η^5-Trimethylsilylcyclopentadienyl)carbonyl(triphenylphosphine)iridium (6). Chlorotrimethylsilane (11.5 mL, 90.8 mmol) was added to a suspension of cyclopentadienyl sodium (8.0 g, 91 mmol) in hexane and the mixture was stirred at room temperature for 1 h. The suspension was filtered through Celite in a Schlenk filter and 60.6 mL (97.0 mmol) of 1.6 M n-butyllithium was added by syringe with rapid stirring. A white suspension formed immediately. This mixture was filtered in a Schlenk frit and the solid was dried under high vacuum, giving 10.37 g of trimethylsilylcyclopentadienyl lithium as a white powder (79% yield).

Trimethylsilylcyclopentadienyl lithium (0.50 g, 3.5 mmol) and *trans*-chlorocarbonylbis(triphenylphosphine)iridium (0.80 g, 1.0 mmol) were refluxed under an inert atmosphere in 50 mL of benzene for 5 days. The solution was allowed to cool and filtered through a Florisil-Celite plug. The solution was concentrated to ca. 5 mL, 20 mL of hexane was added and the solution was then placed in a freezer at −15 °C for 4 days. Large cubic orange crystals (0.43 g, 69% yield, m.p. 110 °C) were collected. Anal. Calcd for $C_{27}H_{28}OPSiIr$: C, 52.32; H, 4.55. Found: C, 52.47; H, 4.51. ^1H NMR ($CDCl_3$): δ 7.80−7.28 (m, 15 H, aromatic), 5.06 (t, 2 H, C_5H_4), 4.82 (m, 2 H, C_5H_4), 0.21 (s, 9 H, CH_3). FTIR (CH_2Cl_2): ν_{co} 1923.0 cm^{-1}. MS: *m/e* 620, 618 (M^+); 592, 590 $(M - CO)^+$; 262 $(PPh_3)^+$, 28 $(CO)^+$. ^{31}P NMR (CH_2Cl_2): δ 16.46 (s).

(η^5-Chlorocyclopentadienyl)carbonyl(triphenylphosphine)iridium (12). (Chlorocyclopentadienyl)thallium[19] (0.90 g, 3.0 mmol) and chlorotricarbonyliridium (0.77 g, 2.5 mmol) were refluxed in 50 mL of benzene for 3 days. The benzene was removed under vacuum and the oily solid was extracted with hexane to give a yellow solution. The solution was concentrated to ca. 5 mL and then passed through a hexane-packed alumina column. Elution with hexane gave a single yellow band which was microdistilled. A bright yellow oil (0.65 g) **11** was obtained. The oil (0.60 g, 1.7 mmol) was then refluxed with triphenylphosphine (0.50 g, 1.9 mmol) in 50 mL of benzene for 3 days, filtered through a Florisil−Celite plug, and concentrated to ca. 5 mL. Hexane (20 mL) was added and the solution placed in the freezer at −15 °C for 1 week. A yellow powder was obtained (0.22 g, 20% yield). The solid was placed on a dry packed alumina column, and a yellow band was eluted with a mixture of 25/75 CH_2Cl_2/hexane. The collected band was then passed through a silica column and the product was crystallized from CH_2Cl_2/hexane as yellow needle crystals (mp 107 °C). NMR analysis indicated that the product was very slightly contaminated with (η^5-cyclopentadienyl)carbonyl(triphenylphosphine)iridium. Anal. Calcd for $C_{24}H_{19}OClPIr$: C, 49.53; H, 3.29. Found: C, 50.44; H, 3.51. ^1H NMR ($CDCl_3$): δ 7.87−7.31 (m, 15 H, aromatic), 5.36 (t, 2 H, C_5H_4), 4.94 (t, 2 H, C_5H_4). FTIR (CH_2Cl_2): ν_{co} 1934.3 cm^{-1}. MS: *m/e* 584, 582 (M^+); 556, 554 $(M - CO)^+$; 519, 517 $(M - CO - Cl)^+$; 262 $(PPh_3)^+$; 28 (CO). ^{31}P NMR (CH_2Cl_2): δ 15.91 (s).

(η^5-Benzoylcyclopentadienyl)carbonyl(triphenyl-

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phosphine)iridium (4). Cyclopentadienylsodium (5.0 g, 57 mmol) and methyl benzoate (7.7 g, 57 mmol) were refluxed in 100 mL of THF overnight. The THF was removed to yield a light tan solid upon trituration in hexane. The solid was collected on a Schlenk frit and dried under high vacuum.[17,20] The resulting (benzoylcyclopentadienyl)sodium (0.80 g, 4.2 mmol) was refluxed with *trans*-chlorocarbonylbis(triphenylphosphine)iridium (0.80 g, 1.0 mmol) in 50 mL of benzene for 4 days. The solution was allowed to cool and filtered through a Florisil–Celite plug. After concentrating the solution to ca. 5 mL, 20 mL of hexane was added and the solution was placed in the freezer at −15 °C for five days. An oily residue precipitated and a yellow solution remained. The oily residue under a vacuum gave a foam which yielded 0.2 g (30% yield) of yellow powder upon trituration with pentane. This product was placed on a dry-packed column of alumina and eluted with a 50/50 mix of hexane/methylene chloride, yielding three bands: yellow, red, and orange. The orange band contained the major product. The solvent was removed and crystallization was attempted from methylene chloride and hexane. An orange powdery solid separated from the solution. Further attempts at crystallization were unsuccessful. The powder was placed under high vacuum and warmed gently (35 °C) for 48 h; mp 42 °C. Anal. Calcd for $C_{31}H_{24}O_2PIr$: C, 57.13; H, 3.71. Found: C, 57.05; H, 3.64. ^1H NMR ($CDCl_3$): δ 7.92–7.18 (m, 20 H, aromatic), 5.51 (t, 2 H, C_5H_4), 5.14 (t, 2 H, C_5H_4). FTIR (CH_2Cl_2): ν_{co} 1942.1, 1623.1, and aromatic C–H stretch 3059.3 cm^{-1}. MS: *m/e* 652, 650 (M^+); 624, 622 $(M - CO)^+$; 519, 517 $(M - CO - COC_6H_5)$. ^{31}P NMR (CH_2Cl_2): δ 14.26 (s).

(η^5-Cyanocyclopentadienyl)carbonyl(triphenylphosphine)iridium (10). (Cyanocyclopentadienyl)thallium was prepared by a modification of literature procedures.[21–23] Dry ice (500 g) was added in small portions over a period of 4 h to cyclopentadienyllithium (25.0 g, 0.347 mol) in 400 mL of diethyl ether under nitrogen. The white suspension was diluted with 200 mL water and acidified. After stirring overnight, the white solid (Thiele's acid dimer) was collected and dried (15 g, 39% yield). Dimeric acid (10.8 g, 49.1 mmol) was then suspended in ethyl ether and 9.9 mL (98.2 mmol) of thionyl chloride was added. The suspension was cooled to 0 °C and 5.3 mL (98.2 mmol) of pyridine in 30 mL of ethyl ether was added dropwise over 1 h with rapid stirring. The solid turned light brown and became moisture sensitive.[21] The dimeric acid chloride was suspended in hexane and gaseous ammonia was bubbled through the solution. The solid was collected and dried. The resulting dimeric amide (8.0 g, 37 mmol) was placed in a round bottom flask with 15 mL (excess) of dry pyridine and 14.9 mL (excess) of benzenesulfonyl chloride and heated to 100 °C for 1 h. The mixture was cooled, diluted with water, and extracted with ether. The ether extracts were combined and washed with dilute aqueous acid and then dilute KOH and dried over magnesium sulfate. The solvent was removed, giving 3.3 g (48% yield) of the dimeric nitrile.[22] The dimeric nitrile was thermally cracked (neat, 200 °C and 22 mmHg) and distilled into a receiver flask which contained 50 mL of hexane with 1.0 mL (14 mmol) of thallium ethoxide. (Cyanocyclopentadienyl)thallium precipitated spontaneously.[23]

(Cyanocyclopentadienyl)thallium (0.35 g, 1.2 mmol) was refluxed with 0.71 g (0.94 mmol) of *trans*-chlorocarbonylbis(triphenylphosphine)iridium in 50 mL of benzene for 4 days. The product was filtered through a Florisil–Celite plug and pumped to dryness. Most of the starting material **4** was recovered, but extraction with CH_2Cl_2 gave a trace amount of material which showed both nitrile and terminal carbonyl stretching vibrations in the IR spectrum. Removal of the solvent left a yellow solid that was purified by column chromatography on alumina with elution occurring in 50/50 CH_2Cl_2/hexane. The yellow solid (0.05 g, 10% yield, mp 121 °C, dec) was analyzed by ^1H NMR, FTIR, ^{31}P NMR, and mass spectrometry. ^1H NMR ($CDCl_3$): δ 7.75–7.32 (m, 15 H, aromatic), 5.77 (t, 2 H, C_5H_4), 5.45 (t, 2 H, C_5H_4). FTIR (CH_2Cl_2): ν_{co} 1953.8 cm^{-1}, ν_{CN} 2162.2 cm^{-1}. MS: *m/e* 573, 571 $(M)^+$; 547, 545 $(M - CN)^+$; 545, 543 $(M - CO)^+$; 262 $(PPh_3)^+$; 28 $(CO)^+$. ^{31}P NMR (CH_2Cl_2): δ 13.75 (s).

(η^5-Formylcyclopentadienyl)carbonyl(triphenylphosphine)iridium (15). (Formylcyclopentadienyl)sodium[24,25] (0.50 g, 4.3 mmol) and *trans*-chlorocarbonylbis(triphenylphosphine)iridium (0.80 g, 1.0 mmol) were refluxed in 50 mL of benzene for 4 days. The solution was allowed to cool and passed through a Florisil–Celite plug. The dark orange solution was concentrated to ca. 5 mL, 20 mL of hexane was added, and the solution was then placed in the freezer at −15 °C for 3 days. The yellow powder obtained was analyzed by ^1H NMR; integration showed contamination in the aromatic region. All attempts at purification by crystallization or chromatography led to decomposition. However, spectroscopic data obtained from the crude product by FTIR, ^{31}P NMR, and ^1H NMR spectrometry are consistent with the expected values. ^1H NMR ($CDCl_3$): δ 9.51 (s, 1 H, CHO), 7.75–7.30 (m, 15 H, aromatic), 5.55 (t, 2 H, C_5H_4), 5.06 (t, 2 H, C_5H_4). FTIR (CH_2Cl_2): ν_{co} 1945.9, 1651.7 cm^{-1}. ^{31}P NMR (CH_2Cl_2): δ 13.71 (s).

[η^5-(Dimethylamino)cyclopentadienyl]carbonyl(triphenylphosphine)iridium (7). [(Dimethylamino)cyclopentadienyl]lithium was prepared by a modification of the original procedure of Boche et al.[26–28] *N,N*-Dimethylhydroxylamine hydrochloride (10.0 g, 102 mmol) and 7.0 mL (90 mmol) of methanesulfonyl chloride in 150 mL of CH_2Cl_2 were placed in a flask and cooled to −35 °C. Triethylamine (28.57 mL, 380 mmol) in 70 mL of CH_2Cl_2 was added dropwise over a period of 4 h. The solution was placed on an ice bath for 30 min. Ice–water (500 mL) was added to the solution in a separatory funnel and the mixture shaken. The layers were separated and the aqueous layer was extracted with two 100-mL portions of CH_2Cl_2. The organic layers were combined and the solvent removed at 0 °C or below via a rotary evaporator to give a yellow oily residue of *N,N*-dimethyl-*O*-(methanesulfonyl)hydroxylamine.[29] The residue was taken up in 75 mL of ethyl ether and dried over anhydrous magnesium sulfate. The solution was filtered and cooled to −78 °C for 2 h. White needle crystals of *N,N*-dimethyl-*O*-(methanesulfonyl)hydroxylamine were collected and dried in a vacuum (8.8 g, 63 mmol, 62% yield).[26,30] These crystals were combined with 4.37 g (62.5 mmol) of cyclopentadienyllithium in 100 mL of THF at −78 °C and the reaction mixture allowed to stir for 1 h. This solution was extremely air, moisture, and temperature sensitive. The solution was then allowed to warm to −20 °C

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(29) **Caution**: We have repeated this procedure several times with no difficulties. However, in one run at 2-fold scale, removal of the CH_2Cl_2 in the cold resulted in a product that darkened rapidly, fumed, and underwent a violent explosion (Kucht, A.; Flores, J. C.; Rausch, M. D., unpublished studies). We therefore recommend that extreme caution (use of fume hood, maintenance of ice temperature, protective face shield, gloves, etc.) be used in handling this material.

(30) The thermal stability of the crystalline *N,N*-dimethyl-*O*-(methanesulfonyl)hydroxylamine is not well-established in the literature. However, in view of the above result, we recommend suitable precautions in its handing. The relative instability of some related compounds have been discussed.[27,31,32]

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and the THF was removed in a high vacuum. Some of the (dimethylamino)-1,3-cyclopentadiene was lost in the removal of the THF as shown by the red decomposition color in the vacuum line. Cold pentane was added to the oily solid and the extract was transferred by a cannula fitted with filter to a flask cooled to −35 °C. *n*-Butyllithium (20 mL of 1.6 M) was added to the solution at −35 °C generating a white solid. This solid was collected, washed with three 20-mL portions of pentane, and dried in high vacuum. The solid, [(dimethylamino)cyclopentadienyl]lithium (3.45 g, 48% yield), was pyrophoric in air.[28]

[(Dimethylamino)cyclopentadienyl]lithium (0.50 g, 4.3 mmol) in 40 mL of THF was transferred by cannula to a benzene solution of 0.75 g (0.96 mmol) of *trans*-chlorocarbonylbis(triphenylphosphine)iridium at 3 °C and the mixture stirred for 1 h. The solution darkened but the latter starting material was largely insoluble under these conditions. The mixture was allowed to return to room temperature and then heated at reflux for 2 days. All the solvent was removed. The residue was extracted with CH_2Cl_2 and then filtered. The solution was concentrated to ca. 10 mL, 35 mL of hexane was added, and the solution then placed in the freezer at −15 °C for 4 days. A solid precipitated but was not the desired product. The remaining solution was filtered, silica (1.0 g) was added, and the solvent was removed. The resulting solid was chromatographed on a dry-packed silica column and eluted with solvents of gradually increasing polarity. At an 85/15 ratio of CH_2Cl_2/THF a dark yellow band was collected that contained the desired product was well as decomposition products. The solvent was removed under vacuum and the oily yellow solid dissolved in a minimal amount of CH_2Cl_2. Hexane was added until the solution started to become cloudly and it was then placed in a freezer at −15 °C for 4 days. The product is highly soluble in both hexane and pentane and all attempts to obtain an analytically pure sample were unsuccessful. ^{1}H NMR ($CDCl_3$): δ 7.80−7.30 (m, 15 H, aromatic), 4.87 (t, 2 H, C_5H_4), 4.42 (t, 2 H, C_5H_4), 2.47 (s, 6 H, NMe_2). FTIR (CH_2Cl_2): ν_{co} 1911.7 cm^{-1}. ^{31}P NMR (CH_2Cl_2): δ 16.07 (s).

As an alternate route to the product prepared above, [(dimethylamino)cyclopentadienyl]dicarbonyliridium[33] (0.05 g, 0.1 mmol) was reacted with 0.04 g (0.1 mmol) of triphenylphosphine in refluxing benzene (10 mL). The solvent was removed and the product analyzed by ^{1}H NMR, ^{31}P NMR, and FTIR. The spectral results obtained were consistent with the values obtained above.

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