Journal of Organometallic Chemistry, 60 (1973) 179–188

THE PREPARATION AND PROPERTIES OF METALLOFLUORENE COMPLEXES OF TRANSITION METALS

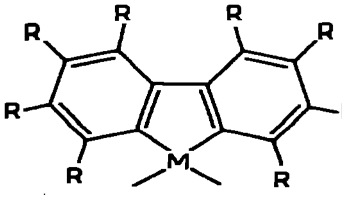
SYLVIA A. GARDNER, HENRY B. GORDON and MARVIN D. RAUSCH*
Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01002 (*U.S.A.*)
(Received February 6th, 1973)

SUMMARY

Metallofluorene complexes $(\pi\text{-}C_5H_5)M(CO)(C_{12}H_8)$ (IVa)–(IVc) and $(\pi\text{-}C_5H_5)M(CO)(C_{12}F_8)$ (IVd)–(IVf) (M = Co, Rh and Ir) have been prepared from reactions of the appropriate (π-cyclopentadienyl)carbonylmetal diiodides with 2,2'-dilithiobiphenyl (IIa) and 2,2'-dilithiooctafluorobiphenyl (IIb), respectively. The triphenylphosphine substitution reactions of cobalt compounds (IVa) and (IVd) have also been studied. Reactions of (IIa) and (IIb) with norbornadieneplatinum dichloride result in the preparation of metallocyclic platinum compounds $(\pi\text{-}C_7H_8)Pt(C_{12}H_8)$ and $(\pi\text{-}C_7H_8)Pt(C_{12}F_8)$. A reaction of (IIb) with zirconocene dichloride produces $(\pi\text{-}C_5H_5)_2Zr(C_{12}F_8)$, the first example of a zirconium-containing metallofluorene.

RESULTS AND DISCUSSION

Although metallofluorene complexes** of structure (I) are known for a variety of Main Group elements[1–11], the synthesis and properties of analogs in the Transition Metal series has been limited to several derivatives of titanium and hafnium[5,12,13].



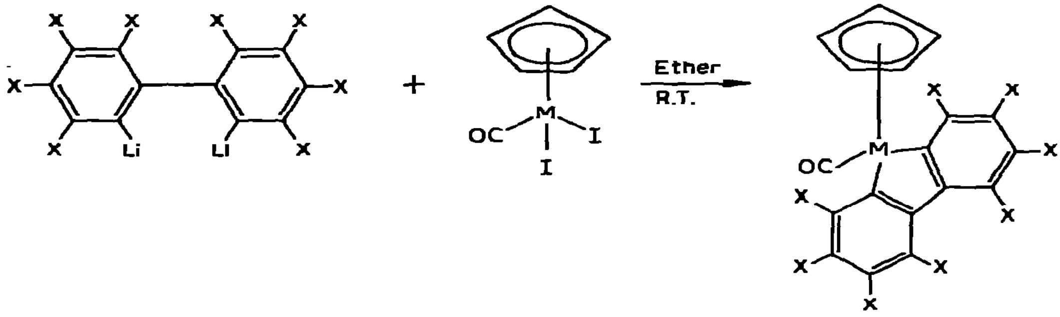
(I)

---

* To whom all correspondence should be addressed.

** Compounds with the structure (I) are called dibenzometalloles. The nomenclature adopted for the metallocyclopentadienes is thus made directly applicable to these systems by simply noting the presence of the two fused benzene rings with a dibenz(o)-prefix. This convention was recommended by *Chemical Abstracts* in 1958 to describe the first member of this class of compounds, 5,5-diphenyldibenzosilole, prepared by Gilman and Gorsich[4,25].

We now report the formation of a series of such compounds (IVa)–(IVf) containing cobalt, rhodium or iridium in the metallocyclic ring by allowing a dianion of Type (II) to react with a suitable organometallic diiodide (IIIa)–(IIIc).



(IIa), X = H
(IIb), X = F

(IIIa), M = Co
(IIIb), M = Rh
(IIIc), M = Ir

(IVa), M = Co, X = H
(IVb), M = Rh, X = H
(IVc), M = Ir, X = H
(IVd), M = Co, X = F
(IVe), M = Rh, X = F
(IVf), M = Ir, X = F

The isolation of complexes (IVa)–(IVc) was effected in yields of 31 %, 3 % and 0.4 %, respectively, when (IIa) was used as the dilithium reagent in reactions with compounds (IIIa)–(IIIc). All three complexes were isolated as lightly colored, air stable solids, although (IVa) was found to be moderately air sensitive while in solution. Compounds (IVd)–(IVf) were prepared by the reactions of dianion (IIb) with diiodides (IIIa)–(IIIc). Complex (IVd), unlike (IVa), was found to be remarkably stable to the air both in solution and in the solid state. The same marked decrease in yields observed in preparations of compounds (IVa)–(IVc) in comparing the Co, Rh and Ir reactions was also noted in this second set of reactions, where the yields were observed as 49 %, 20 % and 4 % for compounds (IVd)–(IVf). We have also noted a similiar variation of yields *versus* central metal atom in studies of reactions of the triphenylphosphine substitution products of compounds (IIIa)–(IIIc) with the dianion formed by the interaction between diphenylacetylene and lithium[14].

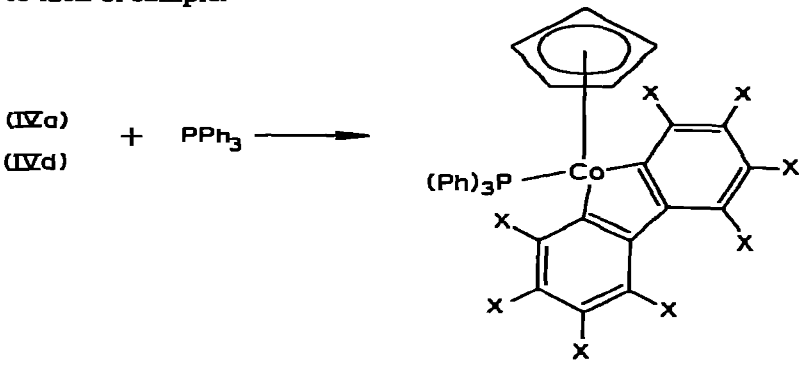
Selected IR and NMR spectral data for complexes (IVa)–(IVf) are summarized in Table 1. A comparison of the NMR spectra of these compounds indicates that unlike the (π-C_5H_5)M(CO)$_2$ complexes (M = Co, Rh and Ir), where the deshielding of the π-C_5H_5 protons is similiar to that seen in the ferrocene, ruthenocene and osmocene series[17], the metallocyclic compounds (IVa)–(IVf) are observed to follow a more varied pattern. Both rhodium-containing metallofluorene compounds isolated, (IVb) and (IVe), show decreased shielding of the π-C_5H_5 ring protons relative to the cobalt compounds (IVa) and (IVd), respectively. However, while this deshielding is of the same order and magnitude observed in the iron-group metallocene spectral comparisons, the differences resulting from changing the metal from rhodium to iridium show opposite shielding effects for the two new iridicycles. Further conclusions based on these observations must await data on the relative reactivities of compounds (IVa)–(IVf).

TABLE 1

Compound	$\nu(CO)$ (cm^{-1})[a]	π-C_5H_5 (τ ppm)[b,c]
$(\pi\text{-}C_5H_5)Co(CO)_2$	2037, 1965[d,e]	4.94
$(\pi\text{-}C_5H_5)Rh(CO)_2$	2051, 1987[d,e]	4.56
$(\pi\text{-}C_5H_5)Ir(CO)_2$	2037, 1957[d,e]	4.45
$(\pi\text{-}C_5H_5)Co(CO)I_2$	2076[f]	4.32
$(\pi\text{-}C_5H_5)Rh(CO)I_2$	2091[f]	3.95
$(\pi\text{-}C_5H_5)Ir(CO)I_2$	2070[f]	4.00
$(\pi\text{-}C_5H_5)Co(CO)(C_{12}H_8)$	2032[g]	4.83
$(\pi\text{-}C_5H_5)Rh(CO)(C_{12}H_8)$	2050[g]	4.42
$(\pi\text{-}C_5H_5)Ir(CO)(C_{12}H_8)$	[h]	4.53
$(\pi\text{-}C_5H_5)Co(CO)(C_{12}F_8)$	2066[g]	4.47
$(\pi\text{-}C_5H_5)Rh(CO)(C_{12}F_8)$	2075[g]	4.15
$(\pi\text{-}C_5H_5)Ir(CO)(C_{12}F_8)$	2053[g]	4.10

[a] Calibrated *versus* polystyrene. [b] Taken in $CDCl_3$. [c] Calibrated using sideband technique. [d] Ref. 15. [e] Ref. 16. [f] Taken in methylene chloride. [g] Taken in carbon tetrachloride. [h] Insufficient sample available for measurement.

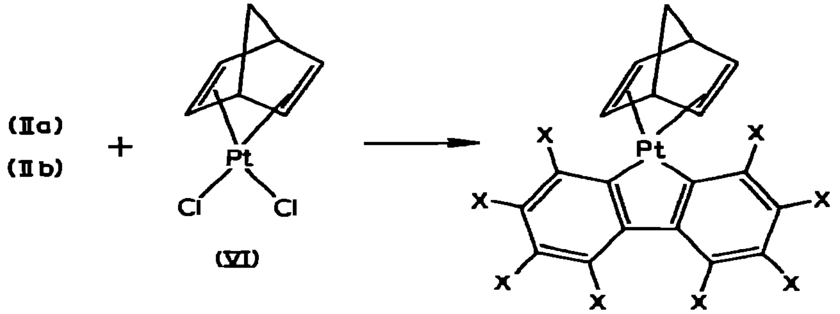
Schuster–Wolden and Basolo[15] have reported on the variation of carbonyl stretching frequencies of the $(\pi\text{-}C_5H_5)M(CO)_2$ compounds (M=Co, Rh and Ir) with a change of the central metal atom, and have correlated their data with kinetic studies of the reaction $(\pi\text{-}C_5H_5)M(CO)_2 + PPh_3 \rightarrow (\pi\text{-}C_5H_5)M(CO)(PPh_3)$. We find that the carbonyl stretching frequencies of our two new series of metallofluorenes follow this same trend, where the two rhodium complexes are observed to exhibit a CO stretch in solution which is higher than that observed for either the cobalt or iridium complexes. Triphenylphosphine substitution reactions have been carried out on compounds (IVa) and (IVd) with formation of complexes (Va) and (Vb), however, similiar reactions involving the rhodium and iridium analogues were not studied owing to lack of sample.



(Va), X = H

(Vb), X = F

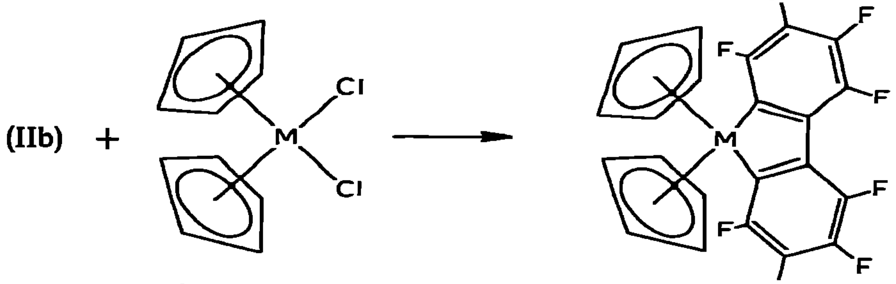
Dianions (IIa) and (IIb) have also proved useful in the preparation of metallofluorene derivatives of several other metals in the transition series. When (IIa) or (IIb) are caused to react with norbornadieneplatinum dichloride (VI), platinafluorene complexes (VIIa) and (VIIb) are produced in yields of 10% and 3.6%, respectively.



(VI)

(VIIa) X = H
(VIIb) X = F

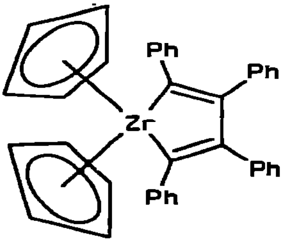
A similar reaction of (IIb) with zirconocene dichloride (VIIIa) has resulted in the isolation of compound (IXa). Although Braye *et al.*[18] have previously reported the preparation of zirconacycle (X), complex (IXa) is, to our knowledge, the first example of a zirconium-containing metallofluorene. The hafnium analogue of (IXa), metallocycle (IXb), has been prepared and described in a previous paper[13],



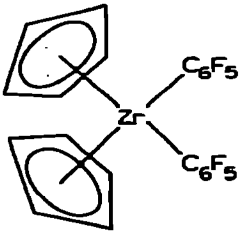
(VIIIa), M = Zr
(VIIIb), M = Hf

(IXa), M = Zr
(IXb), M = Hf

and it is interesting to note that zirconium compound (IXa) is found to be more susceptible to hydrolysis than (IXb). Like the hafnium analogue, however, (IXa) is found to be more hydrolytically stable than its σ-bonded sister, compound (XI)[19].



(X)



(XI)

On storage under nitrogen at room temperature for a period of two months, white crystals were observed to form on the walls of the sample vial containing compound (IXa). These crystals were separated mechanically and identified by a melting point determination as octafluorobiphenyl, m.p. 80° (lit.[20] 79–80°).

EXPERIMENTAL

All operations, including column chromatography, were carried out under a protective dry nitrogen atmosphere using Schlenk tube techniques. Hexane and benzene were dried over calcium hydride and distilled before use. Ethyl ether was distilled from sodium/benzophenone, while tetrahydrofuran (THF) was predried over potassium hydroxide and distilled from sodium-naphthalene. 2,2'-Dibromobiphenyl[21] and 2,2'-dibromooctafluorobiphenyl[20] were prepared by published procedures, as were π-cyclopentadienylcobalt carbonyl diiodide (IIIa)[22], π-cyclopentadienylrhodium carbonyl diiodide (IIIb)[22], π-cyclopentadienyldicarbonyliridium[24,16] and norbornadieneplatinum dichloride[23]. Zirconocene dichloride was obtained from Arapahoe Chemicals. CAMAG neutral alumina was used for column chromatography after heating under vacuum for 3–4 days to remove residual oxygen and water and subsequent deactivation of the alumina with 5% (by weight) of nitrogen-saturated distilled water. Preparative TLC plates were prepared from CAMAG Silica Gel for TLC (5% $CaSO_4$ and UV indicator) and were 20 x 20 cm in dimension with an absorbent thickness of 1.2 mm. NMR and solution IR spectra were obtained on Varian A-60 and Perkin–Elmer 237B instruments, respectively. IR spectra on KBr pellets were taken on a Beckman IR-10. Microanalyses were performed by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts, Amherst, Massachusetts.

Preparation of 2,2'-dilithiobiphenyl (IIa)[25]

2,2'-Dilithiobiphenyl was prepared by the dropwise addition of 12 ml of a 2.38 *M* hexane solution of n-butyllithium (28 mmol) to a stirred solution of 4.0 g of 2,2'-dibromobiphenyl (12.8 mmol) in 40 ml of ethyl ether at 0°. After the addition was complete (15 min) the cooling bath was removed and the reaction mixture allowed to warm to room temperature and stir for 5 h. This solution was then used immediately in further reactions with the π-cyclopentadienylmetal carbonyl diiodides (IIIa)–(IIIc).

Preparation of 2,2'-dilithiooctafluorobiphenyl (IIb)[5]

2,2'-Dilithiooctafluorobiphenyl was prepared at −78° by the dropwise addition of 4.2 ml of a 2.38 *M* hexane solution of n-butyllithium (10 mmol) to a stirred solution of 2.28 g of 2,2'-dibromooctafluorobiphenyl (5 mmol) in 40 ml of ethyl ether. After the addition was complete (15 min) the reaction mixture was stirred for 1 h at −78° and then used immediately in subsequent reactions with the π-cyclopentadienylmetal carbonyl diiodides (IIIa)–(IIIc).

Preparation of π-cyclopentadienyliridium carbonyl diiodide (IIIc)

Using a 50 ml round-bottom flask which had been previously flushed with nitrogen, a solution of 0.5 g $(\pi\text{-}C_5H_5)Ir(CO)_2$[24] (1.6 mmol) in 5 ml ethyl ether was added dropwise to a solution of 0.41 g iodine (1.6 mmol) in 20 ml ethyl ether. The solution slowly turned a lighter red with gas evolution and formation of a red precipitate. The reaction mixture was stirred at room temperature for 18 h, filtered, washed well with methylene chloride and dried, yielding 0.745 g (87%) $(\pi\text{-}C_5H_5)Ir(CO)I_2$ as a red solid. (Found: C, 13.17; H, 0.80; I, 47.00; Ir, 35.48; O, 3.00. $C_6H_5I_2IrO$ calcd.: C, 13.37; H, 0.93; I, 47.08; Ir, 35.65; O, 2.97%). The molecular weight by mass spectrometry was 538–540 (calcd. 538–540 for iridium isotopes 191 and 193). An IR spectrum (KBr) exhibited the following major peaks: 2070s, 1410m, 1000m, 865m cm^{-1}. The NMR spectrum in $CDCl_3$ consisted of a singlet at τ 4.00.

Preparation of 5-(π-cyclopentadienyl)-5-carbonyldibenzocobaltole (IVa)

A slurry of 5.14 g $(\pi\text{-}C_5H_5)Co(CO)I_2$ (IIIa) (12 mmol) in 100 ml ethyl ether was prepared in a 200 ml round-bottom flask which had previously been flamed out under vacuum and flushed with nitrogen. A freshly prepared solution of 12.8 mmol 2,2'-dilithiobiphenyl (IIa) in 40 ml ethyl ether was added dropwise to this suspension over a period of 30 min. The reaction mixture slowly turned dark green and was allowed to stir at room temperature for 24 h. At the end of this period the reaction was filtered under a nitrogen atmosphere to remove a dark precipitate. The resulting green solution was evaporated to dryness under reduced pressure and treated with hexane to induce crystallization of the remaining oil. The dark solid thus obtained was taken up in a minimum amount of benzene and chromatographed on a 1.5 × 35 cm neutral alumina column which had been packed in hexane. Elution with 1/1 benzene/ethyl ether brought down the product as a yellow band which was collected and evaporated to dryness under reduced pressure to yield 1.1 g (31%) of (IVa) as a yellow solid, m.p. 147–151°. An analytical sample was prepared by recrystallization from benzene/hexane followed by drying at 70° *in vacuo*, m.p. 151–155°. (Found: C, 71.05; H, 4.54; Co, 19.40; O, 5.26. $C_{18}H_{13}CoO$ calcd.: C, 71.06; H, 4.31; Co, 19.37; O, 5.26%.) The molecular weight was 304 as determined by mass spectrometry (calcd. 304). An IR spectrum (KBr) exhibited the following major peaks: 2000s, 1420m, 1010m, 820s, 740s cm^{-1}. The NMR spectrum in $CDCl_3$ consisted of a singlet at τ 4.83 (5 H) and a multiplet centered at τ 2.75 (8 H).

Preparation of 5-(π-cyclopentadienyl)-5-carbonyldibenzorhodole (IVb)

A freshly prepared solution of 2,2'-dilithiobiphenyl (12.8 mmol) in 40 ml of ethyl ether was added with stirring over a period of 30 min to a slurry of 5.4 g $(\pi\text{-}C_5H_5)Rh(CO)I_2$ (IIIb) (12 mmol) and 75 ml ethyl ether in a 200 ml flask which had previously been flamed out under vacuum and flushed with nitrogen. The reaction mixture was stirred at room temperature for 24 h and then filtered under a nitrogen atmosphere to remove a dark precipitate. The resulting dark ether solution was evaporated to dryness at reduced pressure and the remaining solid taken up in a minimum volume of methylene chloride and mixed with the small amount of neutral alumina sufficient to form a moist powder. This coated alumina was then dried under vacuum for 1 h at room temperature and poured directly onto the top of a 2.5 × 20 cm neutral alumina column which had been packed dry. Elution with hexane brought down a colorless band which was evaporated to dryness and shown to be 0.5 g biphenyl by TLC, IR, and a mixture m.p. determination. Increasing the polarity of the eluent to 10% benzene in hexane removed a second colorless band from the column. This band was concentrated to near dryness under reduced pressure and filtered to yield 0.14 g (3%) (IVb) as fluffy white needles. An analytical sample was prepared by sublimation at 150°/10^{-4} mmHg m.p. 190–191° dec. (Found: C, 61.94; H, 3.70; O, 4.61; Rh, 29.61. $C_{18}H_{13}ORh$ calcd.: C, 62.08; H, 3.77; O, 4.59; Rh, 29.55%.) The molecular weight was 348 as determined by mass spectrometry (calcd. 348). The following major peaks were observed in the IR spectrum (KBr): 2020s, 1410m, 1040m, 1010m, 800s, 740s cm^{-1}. The NMR spectrum in $CDCl_3$ exhibited a doublet at τ 4.42 [5 H, J(Rh–H) 0.5 Hz] and a multiplet centered at τ 2.75 (8 H).

Preparation of 5-(π-cyclopentadienyl)-5-carbonyldibenzoiridole (IVc)

A slurry of 6.5 g $(\pi\text{-}C_5H_5)Ir(CO)I_2$ (IIIc) (12 mmol) and 75 ml ethyl ether was prepared in a 200 ml flask which had been flamed out under vacuum and flushed with nitrogen. This slurry was then stirred at room temperature while 40 ml of a freshly prepared ethyl ether solution of 2,2′-dilithiobiphenyl (IIa) (12.8 mmol) was added dropwise over a period of 30 min. The red suspension gradually became dark brown. After completion of the addition, the reaction mixture was stirred at room temperature for 24 h and then filtered under nitrogen to remove a dark precipitate. The resulting dark ether solution was evaporated to dryness, taken up in a minimum volume of methylene chloride and mixed with sufficient neutral alumina to form a moist powder. This powder was dried at room temperature for one h and then added to the top of a 2.5 × 15 cm neutral alumina column which had been packed dry. Elution with hexane brought down 0.44 g of biphenyl as a colorless band as evidenced by TLC, IR and a mixed m.p. determination. Increasing the polarity of the eluent to 25% benzene in hexane removed a light yellow band. This was evaporated to yield a red solid, which appeared by TLC to contain the product desired together with a small amount of red impurity of similiar R_f. The red solid was then taken up in a minimal volume of methylene chloride and placed on 2 preparative TLC plates. Three elutions with 15% benzene in hexane separated the product from the red impurity as a colorless band visible under UV light. This band was scraped from the plates, extracted with methylene chloride, filtered and evaporated to dryness, yielding 0.017 g (0.4%) of (IVc) as a white solid. An analytical sample was prepared by recrystallization from benzene/hexane, m.p. 235–236°. (Found: C, 50.33; H, 3.24; Ir, 43.68; O, 3.66. $C_{18}H_{13}IrO$ calcd.: C, 49.41; H, 3.00; Ir, 43.93; O, 3.66%.) The molecular weight determined by mass spectrometry was 436–438 (calcd. 436–438 for iridium isotopes 191 and 193). An IR spectrum (KBr) exhibited the following major peaks: 2000s, 1410m, 1050m, 1020m, 820s, 740s cm^{-1}. The NMR spectrum in $CDCl_3$ consisted of a singlet at τ 4.53 (5 H) and a multiplet centered at τ 2.80 (8 H).

Preparation of 5-(π-cyclopentadienyl)-5-carbonyl-1,2,3,4,6,7,8,9-octafluorodibenzocobaltole (IVd)

$(\pi\text{-}C_5H_5)Co(CO)I_2$ (IIIa) (2.13 g, 5.25 mmol) was added as a solid to a freshly prepared solution of 5 mmol of 2,2′-dilithiooctafluorobiphenyl (IIb) in 40 ml of ethyl ether at −78°. The reaction mixture immediately turned dark green. The cooling bath was then removed and the solution allowed to warm to room temperature and stir for 24 h before filtration under nitrogen to remove a light precipitate. The resulting green solution was evaporated to dryness, taken up in benzene and chromatographed on a 1.5 × 15 cm neutral alumina column which had been packed in hexane.

Elution with benzene brought down a yellow band which was evaporated to dryness to yield 1.1 g (49%) of (IVd) as yellow crystals, m.p. 197–200°. An analytical sample was prepared by recrystallization from methylene chloride/hexane, m.p. 201–203°. (Found: C, 48.05; H, 1.40; Co, 13.10; F, 33.85; O, 3.55. $C_{18}H_5CoF_8O$ calcd.: C, 48.24; H, 1.12; Co, 13.15; F, 33.92; O, 3.57%.) The molecular weight was 448 as determined by mass spectrometry (calcd. 448). The IR spectrum (KBr) consisted of the folowing major peaks: 2060s, 1610m, 1450s, 1350m, 1280m, 1040s, 920m, 850m, 780m, 700 m cm^{-1}. The NMR spectrum in $CDCl_3$ exhibited a singlet at τ 4.47.

Preparation of 5-(cyclopentadienyl)-5-carbonyl-1,2,3,4,6,7,8,9-octafluorodibenzorhodole (IVe)

(π-C_5H_5)Rh(CO)I_2 (IIIb) (2.25 g, 5 mmol) was added as a solid to a freshly prepared solution of 2,2'-dilithiooctafluorobiphenyl (IIb) (5 mmol) in 40 ml ethyl ether at −78°. The cooling bath was then removed and the reaction mixture stirred at room temperature for 48 h. Filtration under nitrogen removed a dark precipitate and the resulting ether solution was evaporated to dryness and taken up in a minimum volume of benzene. This benzene solution was chromatographed on a 1.5 × 30 cm neutral alumina column which had been packed in hexane. Benzene elution brought down a tan band which was reduced to dryness and triturated with ethyl ether to yield 0.5 g (20%) (IVe) as a white solid. An analytical sample was prepared by recrystallization from methylene chloride/hexane, m.p. 221–223°. (Found: C, 43.90; H, 1.19; F, 30.92; O, 3.26; Rh, 20.95. $C_{18}H_5F_8ORh$ calcd.: C, 43.93; H, 1.02; F, 30.88; O, 3.25; Rh, 20.91%.) The molecular weight determined by mass spectrometry was 492 (calcd. 492). The IR spectrum (KBr) exhibited the following major bands: 2060s, 1620m, 1470s, 1360m, 1290m, 1050s, 920m, 830m, 790m, 700m cm^{-1}. The NMR spectrum in $CDCl_3$ consisted of a single peak at τ 4.15.

Preparation of 5-(π-cyclopentadienyl)-5-carbonyl-1,2,3,4,6,7,8,9-octafluorodibenzoiridole (IVf)

(π-C_5H_5)Ir(CO)I_2 (IIIc) (2.70 g, 5 mmol) was added as a solid to a freshly prepared solution of 2,2'-dilithiooctafluorobiphenyl (IIb) (5 mmol) in 40 ml of ethyl ether at −78°. The cooling bath was removed and as the reaction mixture warmed up to room temperature its color slowly changed from red to dark brown. The reaction mixture was stirred at room temperature for 48 h, filtered under nitrogen, and evaporated to dryness. The resulting brown solid was dissolved in a minimum amount of benzene and chromatographed on a 1.5 × 30 cm neutral alumina column which had been packed in hexane. Elution with benzene removed a brown band which was collected and taken to dryness. TLC of the reaction product at this point indicated that the desired compound was present and contaminated with several minor impurities of similiar R_f. The impure iridicycle was thus taken up in a minimal volume of methylene chloride and placed on 4 preparative TLC plates. One elution with 25% benzene in hexane achieved separation of the product as the major colorless band visible under UV light. This band was scraped off the plates, extracted with methylene chloride, filtered, and taken to dryness to produce 0.12 g (4%) (IVf) as white crystals. An analytical sample was prepared by sublimation at 150°/10^{-4} mmHg, m.p. 230–232°. (Found: C, 36.85; H, 1.00; F, 26.01; Ir, 32.91; O, 2.80. $C_{18}H_5F_8IrO$ calcd.: C, 37.18; H, 0.87; F, 26.14; Ir, 33.06; O, 2.75%.) The molecular weight determined by mass spectrometry was 580–582 (calcd. 580–582 for iridium isotopes 191 and 193). An IR spectrum (KBr) exhibited the following major peaks: 2040s, 1610m, 1460s, 1350m, 1290m, 1050s, 920m, 840m, 800m, 700m cm^{-1}. The NMR spectrum in $CDCl_3$ consisted of a singlet at τ 4.10.

Preparation of 5-(π-cyclopentadienyl)-5-triphenylphosphinedibenzocobaltole (Va)

A solution of triphenylphosphine (0.456 g, 1.74 mmol) in 10 ml of methylene chloride was mixed with a solution of (IVa) (0.53 g, 1.74 mmol) in 30 ml methylene chloride in a flask which had previously been flamed out under vacuum and flushed with nitrogen. The reaction mixture was allowed to stand at room temperature for 3 weeks and the orange solution was then concentrated to *ca.* 15 ml and chromatographed on a Florisil column. Elution with ethyl ether removed a yellow band from the column which was evaporated to dryness to yield an orange oil. The oil was treated with a small amount of ether to crystallize it, and filtration yielded 0.30 g (33 %) orange crystals of (Va), m.p. 184–200° dec. An analytical sample was prepared by recrystallization from ethyl ether, m.p. 213–217°. (Found: C, 77.83; H, 5.28. $C_{35}H_{28}CoP$ calcd.: C, 78.06; H, 5.24%.)

Preparation of 5-(π-cyclopentadienyl)-5-triphenylphosphine-1,2,3,4,6,7,8,9-octafluorodibenzocobaltole (Vb)

A solution of triphenylphosphine (0.584 g, 2.23 mmol) in 10 ml of methylene chloride was mixed with a methylene chloride solution (75 ml) of (IVd) (1.0 g, 2.23 mmol) in a flask which had previously been flamed out under vacuum and flushed with nitrogen. The reaction mixture was allowed to stand at room temperature for 2 weeks and the solvent was then removed under reduced pressure to yield an orange brown residue. Recrystallization from warm ethyl ether yielded 0.155 g (10%) of orange crystals (Vb), m.p. 230–232°. (Found: C, 61.50; H, 3.20. $C_{35}H_{20}CoF_8P$ calcd.: C, 61.60; H, 2.95%.) The NMR spectrum in $CDCl_3$ consisted of a singlet at τ 4.74 (5 H) and a multiplet centered at τ 2.81 (15 H).

Preparation of 5,5-norbornadiene-1,2,3,4,6,7,8,9-octafluorodibenzoplatinole (VIIb)

Norbornadieneplatinum dichloride (VI) (1.70 g, 4.75 mmol) was added as a solid to an ethyl ether solution of 4.75 mmol 2,2'-dilithiooctafluorobiphenyl (IIb) at −78°. The cooling bath was then removed from the reaction flask and the contents were allowed to warm to room temperature and stir for 4 h. Filtration of the reaction mixture and evaporation to dryness yielded a red brown oil which was extracted with 1/1 benzene/hexane. The resulting solution was cooled to −20° and filtered, yielding 0.10 g (3.6 %) light brown crystals of (VIIb) which did not melt below 300°. (Found: C, 39.00; H, 1.65; F, 25.95; Pt, 33.30. $C_{19}H_8F_8Pt$ calcd.: C, 39.12; H, 1.38; F, 26.05; Pt, 33.44 %.)

Preparation of 5,5-norbornadienedibenzoplatinole (VIIa)

Complex (VIIa) was prepared in 4.8 % yield by a method similiar to that used for the preparation of compound (VIIb). The product was isolated as light brown crystals, m.p. 200–202°. (Found: C, 52.27; H, 3.75; Pt, 44.19. $C_{19}H_{16}Pt$ calcd.: C, 51.92; H, 3.67; Pt, 44.42 %.)

Preparation of 5,5-di-(π-cyclopentadienyl)-1,2,3,4,6,7,8,9-octafluorodibenzozirconole (IXa)

An ethyl ether solution of 2,2'-dilithiooctafluorobiphenyl (IIb) (5 mmol) was added dropwise to a THF solution (minimum volume) of zirconocene dichloride (VIII) (1.40 g, 4.8 mmol) in a flask which had previously been flamed out under vacuum and flushed with nitrogen. The addition was made at −65°. The reaction mixture was stirred while it was allowed to gradually warm to 0°. The solvent was then removed and the solid residue was washed with ethyl ether and extracted with warm benzene. The extract was concentrated to near dryness and filtered to yield 0.10 g (4%) crystals of (IXa), m.p. 325°. (Found: C, 50.94; H, 2.06; F, 29.30. $C_{22}H_{10}F_8Zr$ calcd.: C, 51.06; H, 1.95; F, 29.37%.) The molecular weight determined by mass spectrometry was 517 (calcd. 517). The NMR spectrum in $CDCl_3$ consisted of a singlet at τ 3.48.

ACKNOWLEDGEMENTS

The authors are grateful to the National Science Foundation for a grant in support of this research program. We also wish to thank Dr. Edmond Samuel for assistance in preparation of the zirconocycle (IXa), and Dr. Alan Siegel for obtaining the mass spectra.

REFERENCES

1 R. Köster and G. Benedikt, *Angew. Chem., Int. Ed. Engl.*, 2 (1963) 323.
2 G. Wittig and W. Herwig, *Chem. Ber.*, 88 (1955) 962.
3 J. J. Eisch and W. C. Kaska, *J. Amer. Chem. Soc.*, 84 (1962) 1501; J. J. Eisch and W. C. Kaska, *ibid.*, 88 (1966) 2976.
4 H. Gilman and R. D. Gorsich, *J. Amer. Chem. Soc.*, 80 (1958) 1883.
5 S. C. Cohen and A. G. Massey, *J. Organometal. Chem.*, 10 (1967) 471.
6 R. Gelius, *Chem. Ber.*, 93 (1960) 1759.
7 G. Wittig and A. Maercker, *Chem. Ber.*, 97 (1964) 747.
8 I. G. M. Campbell, R. C. Cookson, M. B. Hocking and A. N. Hughes, *J. Chem. Soc.*, (1965) 2184.
9 J. Goubeau, T. Kalmar and H. Hofmann, *Justus Liebigs Ann. Chem.*, 659 (1962) 39; O. M. Nefedov and M. N. Manakov, *Izv. Akad. Nauk. SSSR, Otd. Khim Nauk*, (1963) 769; *Chem. Abstr.*, 59 (1963) 8780.
10 G. Märkel and R. Potthast, *Angew. Chem., Int. Ed. Engl.*, 6 (1967) 86.
11 S. C. Cohen, M. L. N. Reddy and A. G. Massey, *J. Organometal. Chem.*, 11 (1968) 563.
12 M. D. Rausch and L. P. Klemann, *Chem. Commun.*, (1971) 354.
13 M. D. Rausch, H. B. Gordon and E. Samuel, *J. Coord. Chem.*, 1 (1971) 141.
14 S. A. Gardner and M. D. Rausch, unpublished studies.
15 H. G. Schuster-Wolden and F. Basolo, *J. Amer. Chem. Soc.*, 88 (1966) 1657.
16 E. O. Fischer and K. S. Brenner, *Z. Naturforsch. B*, 17 (1962) 774.
17 M. D. Rausch and V. Mark, *J. Org. Chem.*, 28 (1963) 3225.
18 E. H. Braye, W. Hübel and I. Caplier, *J. Amer. Chem. Soc.*, 83 (1961) 4406.
19 M. A. Chaudhari and F. G. A. Stone, *J. Chem. Soc. A*, (1966) 838.
20 A. G. Massey, S. C. Cohen, D. E. Fenton and A. J. Tomlinson, *J. Organometal. Chem.*, 6 (1966) 301.
21 H. Gilman and B. J. Gaj, *J. Org. Chem.*, 22 (1957) 447.
22 R. B. King, *Inorg. Chem.*, 5 (1966) 82.
23 E. W. Abel, M. A. Bennett and G. Wilkinson, *J. Chem. Soc.*, (1959) 3178.
24 M. D. Rausch, P. S. Andrews, S. A. Gardner and A. Siegel, *Organometal. Chem. Syn.*, 1 (1971) 289.
25 H. Gilman and R. D. Gorsich, *J. Amer. Chem. Soc.*, 77 (1955) 6380.