Formation and Reactions of a Dirhodium Complex Incorporating a Secondary Phosphine. Intramolecular Proton Transfer, CNR Addition, and Conversion to the Trinuclear Cluster $(\eta\text{-}C_5H_5)_2Rh_2Ir(\mu\text{-}PPh_2)(CO)_2(CF_3C_2CF_3)$

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The reaction of $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}\eta^2\text{-}CF_3C_2CF_3)$ (1) with PPh_2H at room temperature gives the new dinuclear species $(\eta\text{-}C_5H_5)_2Rh_2(CO)(PPh_2H)(\mu\text{-}\eta^1{:}\eta^1\text{-}CF_3C_2CF_3)$ (2). In solution, or in the absence of an atmosphere of CO, facile conversion of 2 to $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1{:}\eta^2\text{-}C(CF_3)C(CF_3)H\}$ (3) occurs via an intramolecular proton shift accompanied by decarbonylation. This process is irreversible. Complex 3 reacts with CNR (R = *i*-Pr, *t*-Bu) to produce the phosphaalkylidene species $(\eta\text{-}C_5H_5)_2Rh_2(CNR)\{PPh_2C(CF_3)C(CF_3)H\}$ (4), presumably via nucleophilic attack of CNR at a Rh center and migration of the alkylidene moiety to the μ-PPh_2 group. Reaction of 2 with *n*-BuLi and subsequently $[Ir(cod)Cl]_2$ yields the new heteronuclear cluster compound $(\eta\text{-}C_5H_5)_2Rh_2Ir(\mu\text{-}PPh_2)(CO)_2(CF_3C_2CF_3)$ (6), which was characterized by X-ray crystallography. Crystal data for 5: monoclinic, $P2_1/c$, $a = 9.728$ (1) Å, $b = 16.020$ (2) Å, $c = 17.649$ (2) Å, $\beta = 91.95$ (3)°, $Z = 4$, final $R = 0.041$ for 5195 "observed" reflections.

Introduction

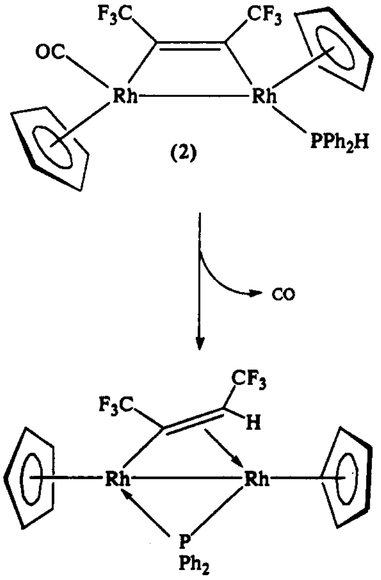
Secondary phosphines (PR_2H) are interesting ligands because they provide options for further reactions that are not available with coordinated tertiary phosphines. For example, a common reaction is oxidative addition of the P–H bond to low-valent metal atoms in polynuclear complexes to form μ-phosphido–hydrido complexes.[1] We have established previously[2] that $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}\eta^2\text{-}CF_3C_2CF_3)$ (1) readily adds a range of tertiary phosphines to give the complexes $(\eta\text{-}C_5H_5)_2Rh_2(CO)(PR_3)(\mu\text{-}\eta^1{:}\eta^1\text{-}CF_3C_2CF_3)$ in quantitative yield. Thus, 1 should be a useful model compound for further investigating the behavior of coordinated secondary phosphines. In this paper, we describe the coordinative addition of PPh_2H to 1 and some subsequent reactions of the product. We also report the formation and characterization of a Rh_2Ir cluster complex from the dinuclear diphenylphosphine species.

Results and Discussion

Formation and Spectroscopic Properties of Dinuclear Complexes. Addition of PPh_2H to a solution of 1 in dichloromethane yields the expected product $(\eta\text{-}C_5H_5)_2Rh_2(CO)(PPh_2H)(\mu\text{-}\eta^1{:}\eta^1\text{-}CF_3C_2CF_3)$ (2) in moderate yield (47%). In contrast to the analogous tertiary phosphine complexes, 2 is unstable in solution; however, the orange solid may be stored under a CO atmosphere for ca. 1 week. Despite this relative instability, purification of the product was achieved by thin-layer chromatography and subsequent recrystallization from pentane and dichloromethane under an atmosphere of CO. Analytical and spectroscopic data are presented in the Experimental Section and support the structure shown. Brief comment on the most structurally significant results is given below.

The asymmetry of the molecule is indicated by two C_5H_5 and two CF_3 resonances in the NMR spectra. The NMR spectra also provide evidence for an intact secondary phosphine ligand. In the ^1H spectrum, the phosphine proton resonance at δ 6.85 is observed as a doublet with a P–H coupling of 243 Hz. The $^{31}P\{^1H\}$ NMR spectrum contains a doublet of quartets at δ 45.4 with couplings to rhodium and fluorine of 174 and ca. 2 Hz, respectively. Absorptions at 2295 (P–H) and 1985 cm^{-1} (CO) in the infrared spectrum support the terminal attachments of the phosphine and carbonyl groups.

A second product was also obtained in substantial yield (31%) from the reaction. From analytical and spectroscopic data, it was formulated as a μ-diphenylphosphido complex, $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1{:}\eta^2\text{-}C(CF_3)C(CF_3)H\}$ (3). It is derived from 2 by an intramolecular 1,3-proton shift accompanied by decarbonylation. Thus, if a solution of 2 is exposed to air, a quantitative yield of 3 is collected after ca. 8 h.



(3)

In contrast to the case for 2, there are no ν(CO) or ν(P–H) absorptions in the infrared spectrum of 3. The ^1H NMR spectrum shows two cyclopentadienyl proton singlets and a one proton multiplet centered at δ 1.68, which is assigned to the proton on the alkylidene unit. The multiplicity of this resonance was not sufficiently well defined for detailed analysis. The related complex $Mn_2(CO)_7(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1{:}\eta^2\text{-}C(CF_3)C(CF_3)H\}$, which incorporates

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[1] See, for example: Powell, J.; Fuchs, E.; Gregg, M. R.; Phillips, J.; Stainer, M. V. R. *Organometallics* 1990, *9*, 387 and references therein.

[2] Dickson, R. S.; Oppenheim, A. P.; Pain, G. N. *J. Organomet. Chem.* 1982, *224*, 377.

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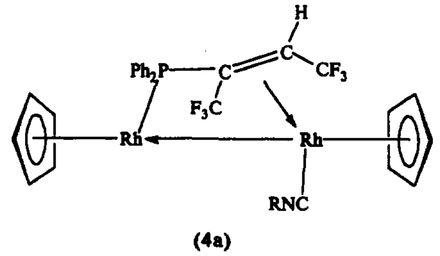
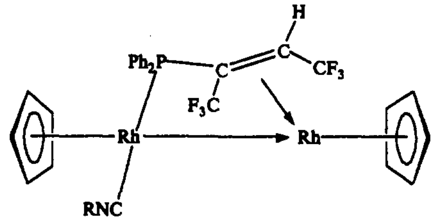
a similar alkylidene moiety, exhibits a doublet of quartets resonance for the appropriate proton in the ^1H NMR spectrum, with F–H and P–H coupling constants of 8.6 and 9.9 Hz, respectively.[3] In the present situation, the additional Rh–H coupling presumably adds to the complexity of the observed resonance. The ^{19}F NMR spectrum of 3 exhibits a quartet at δ 50.5 and a quartet of doublets of doublets at δ 54.9. The F–H coupling constant of 11.0 Hz and the F–F coupling constant of 12.0 Hz present in the high-field resonance fall within the normal ranges of 8–11 (*gem*-$C(CF_3)H$) and 11–15 Hz (*vic,cis*-$C(CF_3)C(CF_3)$), respectively.[4] The additional coupling of ca. 2 Hz is assigned to three-bond Rh–F coupling. The $^{31}P\{^1H\}$ NMR spectrum contains a doublet of doublets at δ 155.1, and the strong coupling (183 and 126 Hz) to both rhodium atoms is consitent with the bridging arrangement of the PPh_2 unit. The large downfield shift of this resonance is characteristic of a three-membered Rh–Rh–P ring.[5]

Complex 3 reacted slowly with CO at atmospheric pressure, but a variety of uncharacterized products were formed in low yields. TLC analysis of the product mixture indicated it did not contain 2. However, treatment of a solution of 3 in dichloromethane with an equimolar amount of *tert*-butyl isocyanide produced the novel dinuclear compound $(\eta\text{-}C_5H_5)_2Rh_2(CN\text{-}t\text{-}Bu)\{PPh_2C(CF_3)C(CF_3)H\}$ in a yield of 65%. An analogous complex was obtained with isopropyl isocyanide. These complexes were characterized from microanalytical and spectroscopic results. Data for the *tert*-butyl complex are discussed below.

There is a strong peak at 2180 cm^{-1} in the infrared spectrum, indicating that the isocyanide is incorporated as a terminally bonded group. The ^1H NMR spectrum shows resonances for the *tert*-butyl and phenyl groups and for two cyclopentadienyl groups; there is an additional one-proton resonance at δ 2.90. This latter resonance appears as a quartet of multiplets and is assigned to the proton in the alkylidene moiety $C(CF_3){=}C(CF_3)H$. Compared to the corresponding resonance in the starting compound 2, this resonance occurs 1.22 ppm further downfield. The assignment is supported by the ^{19}F NMR spectrum. The $^{31}P\{^1H\}$ NMR spectrum is unusual and features a doublet of doublets of quartets of multiplets resonance at δ 16.5. The doublets are attributed to one- and three-bond couplings to rhodium (160 and 85 Hz, respectively), and the well-defined quartet is assigned to a three-bond phosphorus to fluorine coupling of 4 Hz. We assign the additional multiplicity to unresolved ^4J(F–P) coupling. In the spectrum of the starting complex, the resonance of the bridging phosphido group occurs ca. 139 ppm further downfield at δ 155.1 and does not exhibit any fluorine coupling. The chemical shift and multiplicity of the isocyanide complex are therefore inconsistent with retention of a μ-PPh_2 group but can be explained if the phosphido group has inserted into the rhodium–alkylidene σ-bond to form a bridging alkenylphosphine. There is precedence for a phosphorus nucleophile to attack the alkyne carbon of hexafluorobut-2-yne.[6] Proposed structures for the products $(\eta\text{-}C_5H_5)_2Rh_2(CNR)\{PPh_2C(CF_3)C(CF_3)H\}$ (R = *t*-Bu, *i*-Pr) are shown (**4a,b**). It may be postulated that an isocyanide ligand, being a relatively good π-acceptor, would bond preferentially to the more electron-rich metal. This would favor the structure depicted in **4b**. Unfortunately, crystals of suitable quality for an X-ray diffraction study could not be obtained for either of the isocyanide complexes.

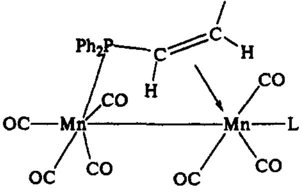


(4a)



(4b)

Similar behavior has been observed[7] on reaction of the dinuclear manganese complex $Mn_2(CHCH_2)(\mu\text{-}PPh_2)(CO)_7$ with either *t*-BuNC or PEt_3. These reactions yield the compounds $Mn_2\{P(Ph)_2CHCH_2\}(CO)_7L$ (L = *t*-BuNC, PEt_3), the structures of which are illustrated by **5**. The PEt_3 derivative was characterized by a single-crystal X-ray structural determination. It is likely that in the present reaction of 3 with CNR, nucleophilic attack of the incoming group at one rhodium center promotes migration of the alkylidene to the phosphorus atom of the phosphido group.



5;L = CNBu^t, PEt_3

Formation of the Rh_2Ir Cluster. The preparation of the dinuclear complex 2 opened up a possible new route to heteronuclear clusters based upon the reaction sequence shown in eq 1. The reaction between 2, 1 equiv of *n*-BuLi,

$$(\eta\text{-}C_5H_5)_2Rh_2(CO)(PPh_2H)(\mu\text{-}\eta^1{:}\eta^1\text{-}CF_3C_2CF_3) \xrightarrow{n\text{-BuLi}} (\eta\text{-}C_5H_5)_2Rh_2(CO)\{PPh_2^-Li^+\}(\mu\text{-}\eta^1{:}\eta^1\text{-}CF_3C_2CF_3) \xrightarrow{ML_nCl} (\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}PPh_2)\{ML_n\}(\mu\text{-}CF_3C_2CF_3) \quad (1)$$

and $[Ir(cod)Cl]_2$ in tetrahydrofuran at −50 °C was carried out under a CO atmosphere. The CO was needed to inhibit the conversion of 2 to 3. When this reaction solution was warmed to room temperature, the color changed from orange to dark red. Some lithium chloride precipitated and was separated by filtration. Three organometallic products were separated upon TLC of the filtrate.

The major product was a deep red solid. Interestingly, this product was formed and could be isolated from the direct reaction of 2 with *n*-BuLi. The red solid appears to be homogeneous, but attempts to characterize it from

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analytical and spectroscopic data (see Experimental Section) have been unsuccessful. It is not the anticipated lithiation intermediate depicted in eq 1, since it does not react with the iridium compound [Ir(cod)Cl]$_2$. The second product was identified spectroscopically as **2** and was isolated in trace yield only.

From the third TLC band, a green product formulated as the new heteronuclear μ-phosphido cluster (η-C_5H_5)$_2$Rh$_2$Ir(μ-PPh$_2$)(CO)$_2$($CF_3C_2CF_3$) (**6**) was isolated in 24% yield. This product is presumably formed via the lithiated phosphine intermediate shown in eq 1. A parent ion is observed in the mass spectrum, and there are prominent peaks corresponding to the successive loss of two carbonyls. The infrared spectrum contains two strong terminal carbonyl absorptions at 2010 and 1965 cm^{-1}. Thus, the cyclooctadiene ligand initially present in the reactant [Ir(cod)Cl]$_2$ has been replaced by two CO groups in the course of the reaction. The $^{31}P\{^1H\}$ NMR spectrum shows a very low field doublet of doublets signal at δ 208.4 with Rh–P couplings of 127 and 11 Hz, and this indicates the presence of a μ-PPh$_2$ ligand. The ^1H and ^{19}F NMR spectra reveal that the cyclopentadienyl and trifluoromethyl environments, respectively, are inequivalent in this cluster. This is consistent with the alkyne unit bridging the Rh–Ir bond. In order to unambiguously determine the nature of all ligand attachments in **6**, an X-ray diffraction study was undertaken.

Crystal and Molecular Structure of (μ-C_5H_5)$_2$Rh$_2$Ir(μ-PPh$_2$)(CO)$_2$($CF_3C_2CF_3$). The molecular structure consists of a triangular arrangement of one Ir and two Rh atoms. The diphenylphosphido ligand bridges the Ir–Rh(1) bond, while hexafluorobut-2-yne bridges the metal face and is σ-bonded to Rh(1) and Ir and π-bonded to Rh(2). The Ir atom is ligated by two terminal CO groups, and one η^5-cyclopentadienyl ring is bonded to each of the Rh atoms.

Within the metal triangle, the Rh(1)–Rh(2) bond length (2.690 (1) Å) is similar to the Rh–Rh bond lengths normally found[8-12] in multinuclear rhodium complexes. The Ir–Rh(1) bond distance (2.716 (1) Å) is statistically significantly longer (0.099 Å) than the Ir–Rh(2) bond length (2.617 (1) Å). However, both values fall within the range established[13-19] for other structurally characterized Rh–Ir complexes. In the present cluster compound, the longer Ir–Rh distance is that which is parallel to the alkyne C(61)–C(71) bond and is bridged by the diphenylphosphido ligand. However, it is not clear whether PPh$_2^-$, $CF_3C_2CF_3$, or both bridging ligands are causing this effect. The metal–phosphorus bond lengths Rh(1)–P (2.263 (2) Å) and Ir–P (2.259 (2) Å) are virtually identical and are shorter than those values calculated as the mean of all observed Rh–phosphide (2.307 Å) and Ir–phosphide (2.355 Å) bonds.[20] Presumably, this difference reflects the flexibility of the μ-phosphido ligand in coordinating two different metal centers. No Rh–P–Ir bridging compounds were available for comparison.

It has been proposed[21-23] that the ^{31}P NMR chemical shift value of a μ-PPh$_2$ group can be used as a diagnostic probe for the presence or absence of metal–metal bonding. Indeed, within the structurally related complexes Fe$_2$(CO)$_6$(μ-PPh$_2$)(μ-X) (X = three-electron donor ligand), the $\delta(^{31}P)$ values have been found to correlate favorably with corresponding M–P–M bond angles and M–M bond lengths.[24] In complex **6**, the angle Ir–P–Rh(1) is acute (73.8 (1)°), and the organophosphido ligand bridges across a metal–metal bond. This may have been anticipated from the very low field ^{31}P chemical shift value (δ 208.4) for the phosphorus.[23,25] However, as this is the first report of the structural characterization of a complex that incorporates a Rh–Ir bond bridged by a μ-PPh$_2$ group, it will not be possible to assess the relationship between $\delta(^{31}P)$ and structural assignments until further such compounds are available for comparison.

The phosphorus atom of the bridging diphenylphosphido ligand lies 0.753 Å above the plane of the metal atoms. This ligand has been shown to be very versatile and shows no preference for bonding either in or out of the plane of the metals. Both arrangements are present in the cluster complex Rh$_3$(μ-PPh$_2$)$_3$(CO)$_5$.[26] In the present cluster, the orientation of the μ-PPh$_2$ group on the same side of the trimetal plane as the hexafluorobut-2-yne moiety results in the Rh(1)–Ir–P plane forming a dihedral angle of 155° with the Rh(1)–Rh(2)–Ir plane.

Parameters within the hexafluorobut-2-yne unit, which is attached to the metal core in the μ_3-(η^2-$\parallel$) bonding mode typical of 48-electron clusters,[27,28] are similar to those found in related clusters characterized by X-ray structure determinations.[11,12]

The cyclopentadienyl rings are essentially planar, with an average Rh–C distance of 2.209 (2) Å. The related C–C distances average 1.39 (2) Å for the ring C(21)–C(25) and 1.43 (2) Å for the ring C(31)–C(35).

Bond distances within the terminal carbonyl groups are normal and are similar for both ligands, with Ir–C distances of 1.904 (8) and 1.853 (8) Å and C–O bond lengths of 1.13 (1) and 1.16 (1) Å. The Ir–C–O (terminal) angles are both close to linear, with values of 175.9 (7) and 177.6 (7)°.

Conclusions

In this study, a range of interesting reaction pathways has been developed based on the initial coordinative addition of the secondary phosphine PPh$_2$H to a dinuclear rhodium complex. The addition product **2** is fairly stable in the solid state, but a facile P–H bond cleavage occurs

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when it is left in solution. An intramolecular H migration converts the μ-η^1:η^1-alkyne to a μ-η^1:η^2-alkenyl group, and the remaining phosphide group occupies a bridging position between the two metal atoms. The resultant product 3 has been characterized spectroscopically. Although this reaction is not reversible, 3 does add isocyanides in solution at room temperature. In these reactions, the CNR ligand attaches to one rhodium, and there is a concomitant condensation of the phosphide and alkenyl groups to form a new bridging phosphaalkylidene group. The conversion of 2 and 3 occurs readily in solution but can be inhibited by keeping the solution under an atmosphere of CO. It is then possible to investigate the reactivity of the intact PPh_2H ligand. By treatment with *n*-BuLi, it is converted to a $PPh_2^-Li^+$ group, which is potentially reactive with a range of halide species. We have shown that the addition of $[Ir(cod)Cl]_2$ results in LiCl elimination and the formation of a bridging phosphido–Rh_2Ir cluster. Thus, we have demonstrated that an interesting range of inter- and intramolecular reactions can be developed based on the initial coordination of a secondary phosphine to a dinuclear complex.

Experimental Section

The general experimental procedures and instrumental techniques have been described in a previous paper.[11] Literature methods were used to prepare $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}\eta^2\text{-}CF_3C_2CF_3)$[29] and $[Ir(cod)Cl]_2$.[30] Commercial samples of the following reagents were used without purification: CO (Matheson); diphenylphosphine, isopropyl isocyanide, and *tert*-butyl isocyanide (Strem); *n*-butyllithium (Aldrich). All reactions and manipulations were done under purified nitrogen with use of standard Schlenk techniques.

Reaction of $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}\eta^2\text{-}CF_3C_2CF_3)$ (1) with PPh_2H. A slight excess of PPh_2H was added to a dichloromethane solution of 1 (0.150 g, 0.285 mmol) at room temperature. The color of the solution immediately changed from green to orange. TLC of the solution with a 1:1 mixture of hexane and dichloromethane as eluent separated five bands. The first, fourth, and fifth bands were present in trace amounts and were not isolated. Extraction of the third band with dichloromethane and evaporation of the solvent gave an orange solid. This was recrystallized from pentane and dichloromethane at −50 °C under an atmosphere of CO to give orange crystals of $(\eta\text{-}C_5H_5)_2Rh_2(CO)(PPh_2H)(\mu\text{-}\eta^1\text{:}\eta^1\text{-}CF_3C_2CF_3)$ (0.095 g, 47%), mp 112 °C dec. Anal. Calcd for $C_{27}H_{21}F_6OPRh_2$: C, 45.5; H, 3.0; F, 16.0; P, 4.4. Found: C, 45.1; H, 3.0; F, 15.8; P, 4.7. Spectroscopic data: IR (CH_2Cl_2) ν(P–H) at 2295 (s) cm^{-1}, ν(CO) at 1985 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.51 (m, 10 H, C_6H_5), 6.85 (d, 1 H, PH, $^1J_{P-H}$ = 243 Hz), 5.43 (d, 5 H, C_5H_5, $^2J_{Rh-H}$ = 1.6 Hz), 5.16 (s, 5 H, C_5H_5); ^{19}F NMR ($CDCl_3$) δ −52.6 (qd, 3 F, CF_3, $^5J_{F-F}$ = 10.8 Hz, $^3J_{Rh-F}$ = 2.3 Hz), −55.4 (qdd, 3 F, CF_3, $^5J_{F-F}$ = 10.8 Hz, $^3J_{Rh-F}$ = 2.3 Hz $\approx$ $^4J_{P-F}$); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 45.4 (dq, PH, $^1J_{Rh-P}$ = 174 Hz, $^4J_{P-F} \approx$ 2 Hz); MS [*m/z* ion (relative intensity)] 712 $[M]^+$ (5), 684 $[M - CO]^+$ (67), 233 $[C_{10}H_{10}Rh]^+$ (100). In the absence of CO, or on standing in solution, $(\eta\text{-}C_5H_5)_2Rh_2(CO)(PPh_2H)(\mu\text{-}\eta^1\text{:}\eta^1\text{-}CF_3C_2CF_3)$ converted to $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}C(CF_3)C(CF_3)H\}$.

The second TLC band also gave this latter complex as an orange-red solid (0.060 g, 31%), mp 125 °C. Anal. Calcd for $C_{26}H_{21}F_6PRh_2$: C, 45.6; H, 3.1; F, 16.7; P, 4.5. Found: C, 46.0; H, 3.4; F, 17.0; P, 4.8. Spectroscopic data: IR (CH_2Cl_2) no ν(P–H) or ν(CO) absorptions observed; ^1H NMR ($CDCl_3$) δ 7.40 (m, 10 H, C_6H_5), 5.35 (s, 5 H, C_5H_5), 5.34 (s, 5 H, C_5H_5), 1.68 (m, 1 H, CF_3H); ^{19}F NMR ($CDCl_3$) δ −50.5 (q, 3 F, CF_3, $^5J_{F-F}$ = 12.0 Hz), −54.9 (qdd, 3 F, CF_3, $^5J_{F-F}$ = 12.0 Hz, $^4J_{H-F}$ = 11.0 Hz, $^3J_{Rh-F}$ = 2 Hz); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 155.1 (dd, μ-PPh_2, $^1J_{Rh-P}$ = 183 Hz, $^3J_{Rh-P}$ = 126 Hz); MS [*m/z* ion (relative intensity)] 684 $[M]^+$ (80), 233 $[C_{10}H_{10}Rh]^+$ (100).

Table I. Summary of Crystal Stucture Data for the Complex $(\eta\text{-}C_5H_5)_2Rh_2Ir(\mu\text{-}PPh_2)(CO)_2(CF_3C_2CF_3)$ (6)

formula	$C_{23}H_{20}F_6O_2PIrRh_2$
mol wt	931.47
cryst syst	monoclinic
space group	$P2_1/c$ (No. 14)
a, Å	9.728 (1)
b, Å	16.020 (2)
c, Å	17.649 (2)
β, deg	91.95 (3)
V, Å^3	2749 (4)
Z	4
D(calcd), g cm^{-3}	2.25
F(000)	1760
μ, cm^{-1}	61.03

Treatment of $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}C(CF_3)C(CF_3)H\}$ with CO. CO gas was bubbled through a solution of $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}C(CF_3)C(CF_3)H\}$ (0.079 g, 0.12 mmol) in dichloromethane (20 mL) for 48 h. The color of the crimson solution did not change over this time. TLC of the reaction mixture separated unchanged starting material (40%) from seven minor bands, which were not characterized. A significant amount of decomposition material remained in the base band.

Reaction of $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}C(CF_3)C(CF_3)H\}$ with *t*-BuNC. Neat *t*-BuNC (0.01 mL, 0.09 mmol) was added to a solution of $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}C(CF_3)C(CF_3)H\}$ (0.064 g, 0.093 mmol) in dichloromethane (15 mL). Within ca. 5 h, the solution color had changed from crimson to bright orange. Evaporation of solvent gave a relatively air-sensitive solid. Recrystallization from pentane at −25 °C under a nitrogen atmosphere gave $(\eta\text{-}C_5H_5)_2Rh_2(CN\text{-}t\text{-}Bu)\{PPh_2C(CF_3)C(CF_3)H\}$ as an orange solid (0.046 g, 65%), mp 128 °C dec. Anal. Calcd for $C_{31}H_{20}F_6NPRh_2$: C, 48.5; H, 3.9; F, 14.9; N, 1.8; P, 4.0. Found: C, 48.3; H, 4.3; F, 14.7; N, 1.7; P, 4.0. Spectroscopic data: IR (CH_2Cl_2) ν(CNR) at 2180 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.81 (m, 2 H, C_6H_5), 7.64 (m, 2 H, C_6H_5), 7.23 (m, 6 H, C_6H_5), 5.11 (s, 5 H, C_5H_5), 5.01 (s, 5 H, C_5H_5), 2.90 (qm, 1 H, CF_3H, $^4J_{F-H}$ = 11.4 Hz), 1.21 (s, 9 H, $C(CH_3)_3$); ^{19}F NMR ($CDCl_3$) δ −50.9 (q, 3 F, CF_3, $^5J_{F-F}$ = 10.8 Hz), −54.1 (dqm, 3 F, CF_3, $^5J_{F-F}$ = 10.8 Hz, $^4J_{H-F}$ = 11.4 Hz); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 16.5 (ddqm, PPh_2, $^1J_{Rh-P}$ = 160 Hz, $^3J_{Rh-P}$ = 85 Hz, $^4J_{F-P}$ = 4 Hz); MS [*m/z* ion (relative intensity)] 767 $[M]^+$ (<10), 684 $[M - CNR]^+$ (25), 233 $[C_{10}H_{10}Rh]^+$ (100).

Reaction of $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}C(CF_3)C(CF_3)H\}$ with *i*-PrNC. Similarly, reaction of $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}C(CF_3)C(CF_3)H\}$ (0.055 g, 0.080 mmol) with *i*-PrNC (>1:1) in dichloromethane (10 mL) lead to the formation of an orange solid after evaporation of solvent from the reaction mixture. Recrystallization from pentane at −25 °C under a nitrogen atmosphere gave $(\eta\text{-}C_5H_5)_2Rh_2(CN\text{-}i\text{-}Pr)\{PPh_2C(CF_3)C(CF_3)H\}$ as an orange solid (ca. 90%). Spectroscopic data: IR (CH_2Cl_2) ν(CNR) at 2150 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.85–7.16 (m, 10 H, C_6H_5), 5.10 (s, 5 H, C_5H_5), 5.01 (s, 5 H, C_5H_5), 3.81 (septet, 1 H, CH, $^2J_{H-H}$ = 6.5 Hz), 2.91 (qm, 1 H, CF_3H, $^4J_{F-H}$ = 11 Hz), 1.18 (d, 3 H, CH_3, $^3J_{H-H}$ = 6.5 Hz), 1.03 (d, 3 H, CH_3, $^3J_{H-H}$ = 6.5 Hz); ^{19}F NMR ($CDCl_3$) δ −51.0 (q, 3 F, CF_3, $^5J_{F-F}$ = 10.4 Hz), −52.0 (dqm, 3 F, CF_3, $^5J_{F-F}$ = 10.4 Hz, $^4J_{H-F}$ = 11 Hz); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 16.7 (ddq, PPh_2, $^1J_{Rh-P}$ = 160 Hz, $^3J_{Rh-P}$ = 85 Hz, $^4J_{F-P}$ = 4 Hz); MS [*m/z* ion (relative intensity)] 753 $[M]^+$ (<10), 684 $[M - CNR]^+$ (25), 233 $[C_{10}H_{10}Rh]^+$ (100).

Reaction of $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}C(CF_3)C(CF_3)H\}$ with *n*-BuLi and $[Ir(cod)Cl]_2$. Under a CO atmosphere, 1 molar equiv of *n*-BuLi in hexane was added to a solution of $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}C(CF_3)C(CF_3)H\}$ (0.054 g, 0.08 mmol) in tetrahydrofuran kept at −50 °C. A solution of $[Ir(cod)Cl]_2$ (0.030 g, 0.05 mmol) in tetrahydrofuran was then added. The resulting orange solution was warmed to room temperature, during which time the color of the solution changed gradually to red-brown. A precipitate of lithium chloride was separated by filtration. The filtrate was taken to dryness and the residue redissolved in a small amount of dichloromethane. TLC with a 8:2 mixture of hexane and diethyl ether as eluent separated five bands from some decomposition material in the base band.

The first band was red and yielded a red solid after extraction and evaporation of solvent. Spectroscopic data: IR (CH_2Cl_2) ν(CO) at 1800 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.30 (m, 10 H, C_6H_5),

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(29) Dickson, R. S.; Johnson, S. H.; Pain, G. N. *Organomet. Synth.* **1988**, *5*, 283.

(30) Herde, J. L.; Lambert, J. C.; Senoff, C. V. *Inorg. Synth.* **1974**, *15*, 18.

Table II. Non-Hydrogen Atom Coordinates and Thermal Parameters for $(\eta\text{-}C_5H_5)_2Rh_2Ir(\mu\text{-}PPh_2)(CO)_2(CF_3C_2CF_3)$

Positional Parameters

atom	x	y	z	U(iso), Å^2	atom	x	y	z	U(iso), Å^2
Ir	0.03516 (3)	0.23797 (2)	0.03281 (1)		C(41)	0.3217 (8)	0.3625 (4)	0.0868 (4)	0.032 (2)
Rh(1)	0.18308 (6)	0.17302 (3)	0.15202 (3)		C(42)	0.2950 (9)	0.4304 (5)	0.0419 (5)	0.046 (2)
Rh(2)	−0.09134 (6)	0.19266 (4)	0.15470 (3)		C(43)	0.3490 (11)	0.5077 (6)	0.0617 (5)	0.059 (2)
F(61)	−0.1595 (8)	0.3992 (4)	0.1863 (4)		C(44)	0.4301 (10)	0.5172 (6)	0.1267 (5)	0.056 (2)
F(62)	−0.1663 (12)	0.3974 (6)	0.0715 (4)		C(45)	0.4610 (11)	0.4497 (6)	0.1720 (5)	0.060(3)
F(63)	−0.0010 (9)	0.4524 (4)	0.1303 (7)		C(46)	0.4035 (9)	0.3730 (5)	0.1533 (4)	0.046 (2)
F(71)	−0.0315 (8)	0.3200 (5)	0.3027 (3)		C(51)	0.3891 (9)	0.2217 (5)	−0.0029 (4)	0.039 (2)
F(72)	0.1593 (10)	0.2636 (4)	0.3143 (3)		C(52)	0.5032 (9)	0.2688 (6)	−0.0211 (5)	0.048 (2)
F(73)	0.1423 (10)	0.3817 (4)	0.2670 (3)		C(53)	0.5990 (12)	0.2383 (6)	−0.0716 (5)	0.061 (3)
P	0.2606 (2)	0.2592 (1)	0.0613 (1)		C(54)	0.5794 (12)	0.1618 (6)	−0.1065 (6)	0.064 (3)
C(21)	0.1636 (10)	0.0396 (6)	0.1920 (5)	0.053 (2)	C(55)	0.4670 (12)	0.1158 (7)	−0.0887 (6)	0.070 (3)
C(22)	0.2113 (11)	0.0902 (6)	0.2522 (5)	0.062 (3)	C(56)	0.3738 (11)	0.1444 (6)	−0.0378 (5)	0.058 (2)
C(23)	0.3403 (12)	0.1233 (7)	0.2345 (6)	0.068 (3)	C(61)	−0.0050 (8)	0.3075 (5)	0.1275 (4)	0.033 (2)
C(24)	0.3667 (12)	0.0920 (7)	0.1634 (6)	0.073 (3)	C(62)	−0.0802 (10)	0.3880 (6)	0.1285 (5)	0.049 (2)
C(25)	0.2586 (10)	0.0405 (6)	0.1364 (5)	0.057 (2)	C(71)	0.0685 (8)	0.2695 (5)	0.1896 (4)	0.031 (1)
C(31)	−0.2085 (11)	0.0738 (6)	0.1555 (5)	0.058 (3)	C(72)	0.0865 (10)	0.3081 (6)	0.2679 (5)	0.051 (2)
C(32)	−0.2819 (11)	0.1325 (6)	0.1119(5)	0.060 (3)	C(1)	0.0237 (9)	0.1384 (5)	−0.0259 (4)	0.038 (2)
C(33)	−0.3125 (12)	0.2033 (7)	0.1588 (6)	0.068 (3)	C(2)	−0.0271 (9)	0.3102 (5)	−0.0429 (4)	0.041 (2)
C(34)	−0.2605 (12)	0.1811 (7)	0.2332 (6)	0.072 (3)	O(1)	0.0127 (7)	0.0772 (4)	−0.0574 (4)	0.063 (2)
C(35)	−0.1974 (11)	0.1049 (7)	0.2309 (6)	0.063 (3)	O(2)	−0.0631 (8)	0.3540 (4)	−0.0921 (4)	0.068 (2)

Anisotropic Thermal Parameters (Å^2)[b]

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ir	0.0302 (1)	0.0240 (1)	0.0226 (1)	−0.0006 (1)	0.0006 (1)	−0.0009 (1)
Rh(1)	0.0302 (3)	0.0226 (3)	0.0361 (3)	−0.0017 (2)	−0.0029 (2)	0.0060 (2)
Rh(2)	0.0314 (3)	0.0314 (3)	0.0271 (3)	−0.0005 (3)	0.0044 (2)	−0.0014 (2)
F(61)	0.109 (6)	0.074 (4)	0.104 (5)	0.039 (4)	0.044 (4)	−0.017 (4)
F(62)	0.255 (12)	0.155 (8)	0.085 (5)	0.162 (9)	−0.059 (6)	−0.036 (5)
F(63)	0.107 (6)	0.030 (3)	0.316 (12)	0.008 (4)	0.074 (8)	0.015 (5)
F(71)	0.096 (6)	0.182 (8)	0.059 (4)	−0.009 (6)	0.020 (4)	−0.060 (5)
F(72)	0.171 (8)	0.099 (5)	0.046 (3)	0.044 (5)	−0.044 (4)	−0.016 (3)
F(73)	0.216 (10)	0.088 (5)	0.055 (3)	−0.087 (6)	0.013 (5)	−0.033 (3)
P	0.032 (1)	0.023 (1)	0.036 (1)	−0.002 (1)	0.002 (1)	0.000 (1)

[a] Estimated standard deviations are given in parentheses. [b] Anisotropic thermal parameters are of the form $\exp[-2\pi^{*2}(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^* + \ldots)]$.

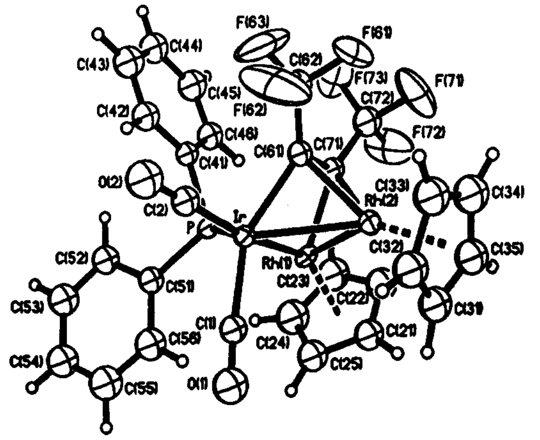

Figure 1. Molecular structure of the complex $(\eta\text{-}C_5H_5)_2Rh_2Ir(\mu\text{-}PPh_2)(CO)_2(CF_3C_2CF_3)$.

Table III. Important Bond Lengths (Å) and Angles (deg) for $(\eta\text{-}C_5H_5)_2Rh_2Ir(\mu\text{-}PPh_2)(CO)_2(CF_3C_2CF_3)$

(a) Bond Lengths

Ir–Rh(1)	2.716 (1)	C(61)–C(71)	1.43 (1)
Ir–Rh(2)	2.617 (1)	Ir–P	2.259 (2)
Rh(1)–Rh(2)	2.690 (1)	Rh(1)–P	2.263 (2)
Ir–C(61)	2.057 (7)	Ir–C(1)	1.904 (8)
Rh(1)–C(71)	2.030 (7)	C(1)–O(1)	1.13 (1)
Rh(2)–C(61)	2.086 (7)	Ir–C(2)	1.853 (8)
Rh(2)–C(71)	2.061 (7)	C(2)–O(2)	1.16 (1)

(b) Bond Angles

Rh(2)–Ir–Rh(1)	60.6 (0)	C(71)–Rh(2)–C(61)	40.2 (3)
Rh(2)–Rh(1)–Ir	57.9 (0)	Ir–C(61)–Rh(2)	78.4 (3)
Ir–Rh(2)–Rh(1)	61.5 (0)	Rh(1)–C(71)–Rh(2)	82.2 (3)
C(1)–Ir–C(2)	96.9 (3)	C(71)–C(61)–C(62)	126.6 (7)
C(1)–Ir–C(61)	152.5 (3)	C(61)–C(71)–C(62)	124.4 (7)
C(2)–Ir–C(61)	100.4 (3)	Ir–P–Rh(1)	73.8 (1)
C(1)–Ir–P	106.6 (3)	Ir–C(1)–O(1)	176.0 (7)
C(2)–Ir–P	110.0 (3)	Ir–C(2)–O(2)	177.6 (7)

5.40 (s, 5 H, C_5H_5), 5.31 (s, 5 H, C_5H_5); ^{19}F NMR ($CDCl_3$) δ −55.25 (s, 9 F, CF_3), −70.4 (m, 1 F, J = 85 Hz), −79.3 (m, 3 F, J = 85 Hz); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 150.4 (ddm, PPh_2, J_{Rh-P} = 176, 125 Hz); MS [m/z ion (relative intensity)] 684 $[C_{26}H_{21}F_6PRh_2]^+$ (10), 664 $[C_{26}H_{20}F_5PRh_2]^+$ (50), 233 $[C_{10}H_{10}Rh]^+$ (100).

The second band was characterized spectroscopically as $(\eta\text{-}C_5H_5)_2Rh_2(CO)(PPh_2H)(\mu\text{-}\eta^1{:}\eta^1\text{-}CF_3C_2CF_3)$. Extraction of the third band and subsequent removal of solvent produced green crystals of $(\eta\text{-}C_5H_5)_2Rh_2Ir(\mu\text{-}PPh_2)(CO)_2(CF_3C_2CF_3)$ (0.010 g, 24%). Spectroscopic data: IR (CH_2Cl_2) ν(CO) at 2010 (s) and 1965 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.42 (m, 10 H, C_6H_5), 5.56 (s, 5 H, C_5H_5), 5.09 (s, 5 H, C_5H_5); ^{19}F NMR ($CDCl_3$) δ −50.05 (q, 3 F, CF_3, $^5J_{F-F}$ = 11.0 Hz), −55.4 (qd, 3 F, CF_3, $^5J_{F-F}$ = 11.0 Hz, $^3J_{Rh-F}$ = 2.8 Hz); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 208.4 (dd, μ-PPh_2, $^1J_{Rh-P}$ = 127 Hz, $^3J_{Rh-P}$ = 11 Hz); MS [m/z ion (relative intensity)] 932/930 $[M]^+$ (43), 904/902 $[M - CO]^+$ (40), 876/874 $[M - 2CO]$ (100), 722/720 $[C_{14}H_{10}F_6OIrRh_2]^+$ (60), 233 $[C_{10}H_{10}Rh]^+$ (90).

X-ray Crystal Structure Analysis of $(\eta\text{-}C_5H_5)_2Rh_2Ir(\mu\text{-}PPh_2)(CO)_2(CF_3C_2CF_3)$ (6). Dark green crystals of 6 were obtained by slow evaporation of a heptane–acetonitrile solution. A crystal of dimensions 0.33 × 0.15 × 0.08 mm was selected and fixed to the end of a Lindeman glass fiber. This was mounted on a Philips PW1100 automatic diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Unit cell parameters were determined from 25 accurately centered reflections and were calculated by the standard Philips program.[31] Crystal data are summarized in Table I. The intensities of 8699 reflections with $6 \leq 2\theta \leq 60°$ were measured using an ω–2θ scan mode with a symmetric scan range of $\pm(1.40 + 0.2 \tan \theta)$ in 2θ

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(31) Hornstra, J.; Stubbe, B. PW1100 Data Processing Program; Philips Research Laboratories, Eindhoven, The Netherlands, 1974.

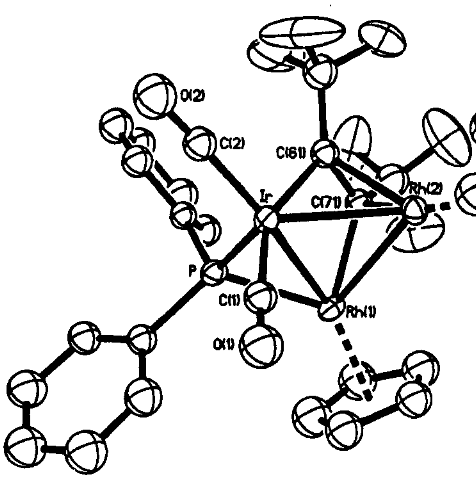

Figure 2. Alternative view of the molecular structure of (η-C_5H_5)$_2$$Rh_2Ir$($\mu$-$PPh_2$)$(CO)_2$($CF_3C_2CF_3$).

from the calculated Bragg scattering angle at a scan rate of 0.06° s^{-1}. Two standard reflections ((600) and (330)) were monitored every 4 h and showed no significant intensity variation. Intensity data were corrected for Lorentz and polarization effects, and a face-indexed numerical absorption correction was applied.[32] This gave 8014 unique reflections, 5195 of which were considered observed with $\{F_o > 6\sigma(F_o)\}$. The space group $P2_1/c$ was uniquely determined by its systematic absences. A three-dimensional Patterson synthesis revealed the position of the iridium atom. A subsequent difference Fourier synthesis phased with this atom located positions of the two rhodium atoms, along with the phosphorus atom. Successive difference Fourier calculations using SHELX-76[32] readily revealed the remainder of the molecular skeleton. Neutral scattering factors were employed for all atoms and were corrected for anomalous dispersion.[33] Anisotropic thermal parameters were introduced for Ir, Rh, and P atoms. Isotropic temperature factors were assigned to all other atoms. Hydrogen atoms were included in their geometrically calculated positions (C–H = 0.97 Å) with a single variable isotropic thermal parameter. The full-matrix least-squares refinement converged at $R = 0.041$ and $R_w = 0.039$ ($R = \sum|F_o| - |F_c|/\sum|F_o|$; $Rw = \sum w^{1/2}(||F_o| - F_c||)/\sum w^{1/2}|F_o|$; $w = 1.37/\sigma^2(F_o)$). The function minimized in the refinement was $\sum w(|F_o| - |F_c|)^2$.[32] No systematic variation of $w(|F_o| - |F_c|)$ with $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The largest peak in the final difference map (1.2 e Å^{-3}) was located 0.95 Å from the Ir atom. The goodness-of-fit value ($[\sum w(|F_o| - |F_c|)^2/(N_{\text{observns}} - N_{\text{params}})]^{1/2}$) was 1.59. All major calculations were performed on a VAX 6800 computer. Views of the molecule along with the atom-numbering scheme are shown in Figures 1 and 2, which were generated using ORTEP.[34] Final positional coordinates are given in Table II. Selected bond lengths and angles are presented in Table III. The supplementary material contains listings of thermal parameters and ligand geometries.

Acknowledgment. This work was assisted by grants from the Australian Research Grants Scheme and the loan of rhodium trichloride from Johnson Matthey. We thank the Australian Government for the award of an Australian Postgraduate Research Award (to O.M.P.). Technical assistance (X-ray crystallography) from Garry Fallon is gratefully acknowledged.

Supplementary Material Available: Listings of bond distances and angles for the ligands and H atom positional parameters (4 pages). Ordering information is given on any current masthead page.

OM9201829

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Half-Open-Titanocene Chemistry: Coupling Reactions of Pentadienyl Ligands with Carbon–Nitrogen and Carbon–Oxygen Multiple Bonds

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The reactions of $Ti(C_5H_5)(2,4\text{-}C_7H_{11})(PEt_3)$ (C_7H_{11} = dimethylpentadienyl) with imines, ketones, and aryl isocyanides have been studied. In each case, the PEt_3 ligand is lost. In the reaction with benzylidenemethylamine, spectroscopic data indicate that coupling of the imine with one end of the 2,4-C_7H_{11} ligand has occurred. With acetone or 3-pentanone, 2 equiv is incorporated, leading to couplings with each end of the open dienyl ligand. A single-crystal X-ray diffraction study has been carried out for the latter. The space group is $P2_1/c$ with $a = 11.467$ (3) Å, $b = 7.647$ (2) Å, $c = 23.981$ (7) Å, $\beta = 92.11$ (3)°, and $V = 2101.3$ Å^3 for $Z = 4$. The structure was refined to discrepancy indices of $R = 0.042$ and $R_w = 0.042$ and revealed σ-allyl coordination as well as evidence for π-alkoxide donation. The reactions with RNC (R = C_6H_5, $p\text{-}CH_3C_6H_4$, $p\text{-}C_2H_5C_6H_4$) were found to lead to the incorporation of 4 equiv of RNC. In each case, two of the isocyanides have, with the pentadienyl ligand, formed a coordinated diazabutadiene ligand and a seven-carbon-atom ring, while the other two have formed an unusual indole which is attached to the former pentadienyl ligand and to an amide which is coordinated to the metal center. For the $p\text{-}C_2H_5C_6H_4NC$ product, the space group is $P\bar{1}$ with $a = 10.858$ (11) Å, $b = 11.103$ (5) Å, $c = 17.552$ (8) Å, $\alpha = 90.35$ (3)°, $\beta = 96.80$ (3)°, $\gamma = 104.28$ (6)°, and $V = 2034.8$ Å^3 for $Z = 2$. The structure was refined to discrepancy indices $R = 0.057$ and $R_w = 0.059$.

Metal pentadienyl compounds have proven to be very versatile in organometallic chemistry[3] and appear to offer particular promise for stoichiometric organic syntheses, whether through coupling reactions[4] or nucleophilic sub-

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