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Synthesis, structure, and reactions of a dimeric rhodium(I) complex with bridging σ- and π-bonded 2,5-dimethylpyrrolido ligands *

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Abstract

Lithium 2,5-dimethylpyrrolide reacts with $[RhCl(CO)_2]_2$ in THF to give the novel dimeric Rh-carbonyl (**1**). The X-ray structure of **1** shows that two $Rh(CO)_2$ moieties are coordinated by two bridging pyrrole rings, where each ring acts as both a σ and a π donor. Reactions of **1** with either PPh_3 (**2**) or $AsPh_3$ (**3**) proceed rapidly and produce yellow air stable compounds. The X-ray structure of **2** confirms that it is a square-planar Rh^I complex with two PPh_3 groups in *trans* positions and the remaining positions occupied by CO and a σ-bonded pyrrolide ion. Corresponding reactions with lithium 2,5-dimethylpyrrolide and $[IrCl(CO)_3]_n$ yield products very similar to compounds **1**–**3**. Preliminary investigations of reactions between $[RhCl(CO)_2]_2$ and the anions of 3,4-dimethylpyrrole and of pyrrole suggested that the products were a mixture of compounds which were not identified.

Introduction

Five-membered aromatic heterocycles like pyrrole (C_4H_5N) or the substituted phospholes ($R,R'C_4H_2P$) [1,2] and arsoles ($R,R'C_4H_2As$) [3] ($R = C_6H_5$, $R' = CH_3$, C_6H_5, etc.) are π-isoelectronic with cyclopentadiene (C_5H_6). They easily can be reduced by alkali metals to form anionic salts such as the cyclopentadiene anion. In view of the similarity in chemical reactivity between these heterocycles and cyclopentadiene, and of the large number of η^5-cyclopentadienyl transition metal com-

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plexes known, one would expect numerous η^5-heterocycle metal complexes to exist. However, surprisingly little is known about organometallic compounds of pyrrole in which the ligand is π- or σ-bonded to the metal, and even less about the corresponding compounds of phosphole and arsole. Metal complexes of such heterocycles that have been investigated are largely restricted to metals of the first row transition series. Some examples of heterocycle metal complexes are e.g., $(\eta^5\text{-}C_4H_4N)Mn(CO)_3$ [4], $(\eta^5\text{-}C_4H_4P)Mn(CO)_3$ [5], $(\eta^5\text{-}C_4H_4N)Fe(\eta^5\text{-}C_5H_5)$ [4,6] or $(\eta^5\text{-}(CH_3)C_4H_4N)Cr(CO)_3$ [7] (for more examples see refs. 8 and 9). In all these cases the ring is deprotonated at the heteroatom and the anionic heterocycle ligand is then coordinated to the metal by either η^5-π bonding or η^1-σ bonding.

Previous studies show [10] that CO substitution reactions of $(\eta^5\text{-}C_4H_4N)Mn(CO)_3$ are orders of magnitude faster than are corresponding reactions of $(\eta^5\text{-}C_5H_5)Mn(CO)_3$. Unfortunately, it was not possible to make a quantitative comparison between the rates of CO substitution of the two compounds, because the cyclopentadienyl compound does not react even after three days at 130 °C [11]. Since the compounds $(\eta^5\text{-}C_5H_5)M(CO)_2$, where M = Co, Rh or Ir, undergo CO substitution reactions at conveniently measured rates [12], we decided to prepare the corresponding $(\eta^5\text{-}C_4H_4N)M(CO)_2$ compounds and determine their rates of reaction. This paper reports our attempts to prepare these compounds by approaches which appeared to be plausible methods of synthesis. The desired compounds were not obtained, but six new compounds were isolated and characterized. The X-ray structures of two rhodium compounds are presented and discussed.

Experimental

Most of the manipulations were carried out with the exclusion of oxygen and moisture, applying usual Schlenk-techniques or using a N_2-filled recirculating glove box (VAC, USA). Tetrahydrofuran, diethyl ether and n-hexane were dried and distilled over Na in the presence of benzophenone under N_2 atmosphere. The n-hexane was stored over concentrated H_2SO_4 was washed with $NaHCO_3$ before distillation.

Chlorodicarbonylrhodium(I) dimer [13], 1-phenyl-2,5-dimethylphosphole [2a], 1-phenyl-2,5-dimethylarsol [3], 3,4-dimethylpyrrole [14] and phenylarsine [15] were prepared by published procedures. Dicobaltoctacarbonyl and chlorotricarbonyliridium were purchased from Strem and used without purification. 2,5-Dimethylpyrrole and pyrrole (Aldrich) were distilled and PPh_3 and $AsPh_3$ (both Aldrich) were recrystallized from methanol prior to use.

^1H, ^{13}C and ^{31}P NMR spectra were recorded on a Varian XL 400 GS and JEOL FX-270 spectrometer. Deuterated solvents were dried and degassed in case of air-sensitive samples. Infrared spectra were recorded on a Perkin–Elmer 283 using KBr pellets, or in case of solution IR using 0.1 mm KBr cells. Mass spectra were obtained at the Analytical Services Laboratory of the Northwestern University on a HP 5985A spectrometer using 70 eV ionization. Elemental analyses were carried out by Galbraith Labs, Inc. (Knoxville, Tennessee, USA).

In the course of this work we observed that the naphthalene radical (with Li^+ or K^+ as counter-cation) cleanly reduces heterocycles such as 2,5- or 3,4-dimethylpyrrole. A typical method of reduction using Li-naphthalide is described here for 2,5-dimethylpyrrole: A solution of 2 g of naphthalene (15.6 mM) in 25 ml THF was added to a mixture of 100 mg lithium (14.15 mM) in 20 ml THF at r.t. and under N_2. The solution, which quickly turned dark green was stirred for 12 h, then 1.4 g of 2,5-dimethylpyrrole (14.7 mM) was slowly added from a syringe. The addition was stopped as soon as the solution was decolorized (after approximately 20 s). The solvent was then removed under oil pump vacuum at ca. 40 °C and the residual solid was washed several times with n-hexane to remove the naphthalene and unreacted organic materials. The remaining lithium salt of the heterocycle anion was generally sufficiently pure for use in the following reactions. Almost quantitative yields of the lithium salts were obtained.

2,5-Dimethylpyrrolyldicarbonylrhodium(I) dimer (1)

Freshly sublimed $[RhCl(CO)_2]_2$ (600 mg, 1.5 mM) was dissolved in 10 ml THF. To this orange solution, at 0 °C under N_2, was added a clear light-yellow solution of Li-2,5-dimethylpyrrolide (312 mg, 3 mM, in 15 ml THF), and the mixture was stirred for 15 min. After evaporation of the solvent the red brown sticky residue was treated with ca. 50 ml of n-hexane, which caused it to form a powder, which then was easily collected on a Schlenk frit, where it was extracted five times with 15 ml portions of diethyl ether to give a clear, red filtrate. The filtrate was then concentrated under vacuum without heating. The flask gradually became cold and then the product precipitated as a green-yellow solid from the dark red solution. At this stage evaporation was stopped and the remaining solvent was removed as completely as possible with a syringe. The solid product was then washed with ca. 5 ml of n-hexane yielding 500 mg (65.8%) of a yellow, air-sensitive powder, m.p. 140 °C (dec.), soluble in THF, DME, diethyl ether, n-hexane and $CHCl_3$ producing red solutions. Anal. Found: C, 38.20; H, 2.95; N, 5.21. $C_{16}H_{16}N_2O_4Rh_2$ calc.: C, 37.96; H, 3.16; N, 5.53%. IR: ν(CO) (KBr): 1976vs, 2041vs; (THF): 1990vs, 2062s; (diethyl ether): 1999vs, 2060vs; (n-hexane): 1999vs, 2059vs; (benzene): 1991vs, 2050vs cm^{-1}.

^1H NMR ($CHCl_3$-d, 22 °C): δ 2.15; 2.20; 2.24 (s, 6); δ 5.61; 5.68; 5.84; 5.95 (s, 2); (C_6H_6-d_6, 25 °C): δ 2.0; 2.2 (s, 6); 5.3; 5.5 (s, 2); (acetone-d_6, 100.0 atom% D, 25 °C) δ 2.0; 2.05; 2.2 (s, 6); 5.41; 5.2 (s, 2). ^{13}C NMR ($CHCl_3$-d, 22 °C): δ 245.3 (CO); 14.3; 16.2; 17.1; 19.5; 22.8 (CH_3 groups); 192.6; 176.9; 134.4; 128.1 (ring). Mass spectrum: m/e (relative intensity). M^+ 506 (3.0); $(M-2CO)^+$ 450 (2.5); $(M-[Rh, 4CO])^+$ 291 (100); $(M-[2CO, pyr\ ^*, Rh])^+$ 253 (13.5); $(M-[3CO, pyr, Rh])^+$ 225 (25.7); $(M-[4CO, pyr, Rh])^+$ 197 (35.0).

For X-ray structure analysis, suitable crystals were grown from a solution mixture of 20 ml diethyl ether and 10 ml n-hexane, containing 30 mg of **1**. The red solution, stored overnight at −20 °C, produced golden-yellow hexagonal shaped crystals.

trans-2,5-Dimethylpyrrolocarbonylbis(triphenylphosphine)rhodium(I) (2)

To a solution of **1** (250 mg, 0.49 mM) PPh_3 (1.5 g, 5.7 mM) was added, with stirring at r.t. under N_2. A reaction readily took place, accompanied by the vigorous evolution of CO and a change in color of the solution from deep red to yellow. The mixture was stirred 5 to 10 min, after which the solvent was removed. The resulting orange-brown solid product was washed first with n-hexane, then several times with

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* pyr = 2,5-dimethylpyrrole.

diethyl ether, yielding a bright yellow air-stable powder, 350 mg (95%), m.p. 194–196 °C (dec.), soluble in DME, THF, chloroform, benzene. Insoluble in n-hexane, diethyl ether and methanol. Anal. Found: C, 67.79; H, 5.20; N, 1.80. $C_{43}H_{38}NOP_2Rh$ calc.: C, 68.9; H, 5.07; N, 1.87%. IR: ν(CO) (KBr): 1968vs; (THF) 1987vs cm^{-1}. ^1H NMR ($CHCl_3$-*d*, 22 °C) δ 1.53 (s, 6H); 5.43 (s, 2H); 7.26 (s, br, 30 H); ^{13}C NMR ($CHCl_3$-*d*, 22 °C) δ 245.3 (CO); 16.74 (CH_3); 106.6 (β-C[ring]); 128.0 (α-C[ring]); 129.6; 132.6; 134.3 (phenyl groups). ^{31}P NMR ($CHCl_3$-*d*, 22 °C) δ values rel. to H_3PO_4 (85%) as an external standard: δ 26.3; 27.1 (d, *J* 139.3 Hz). Mass spectrum, *m/e* (rel. intensity). M^+ 749(52); $(M-\text{pyr})^+$ 655(71); $(M-[\text{pyr, CO}])^+$ 627(18); $(M-PPh_3)^+$ 487(19); $(M-[CO,PPh_3])^+$ 459(100).

Crystals suitable for X-ray analysis were grown by dissolving ca. 50 mg of **2** in a mixture of 20 ml THF and 20 ml DME in a Schlenk flask. The flask was left open to air and the very slow evaporation of the solvents at r.t. resulted in formation of yellow crystals after about one week.

The procedure used for the synthesis of *trans*-2,5-dimethylpyrrolocarbonylbis(triphenylarsine) (**3**) was similar with that of the PPh_3 analogue just described: 200 mg (**1**) (0.39 m*M*); 1.5 g $AsPh_3$ (4.9 m*M*). Reaction time ca. 20 min at r.t. Yield: 300 mg (91.9%). Bright yellow, air stable powder, m.p. 198–200 °C (dec.), moderately soluble in THF, benzene, $CHCl_3$. Insoluble in n-hexane and diethyl ether. Anal. Found: C, 61.48; H, 4.60; N, 1.54. $C_{43}H_{38}NAs_2ORh$ calc.: C, 61.67; H, 4.54; N, 1.67%. IR: ν(CO) (KBr) 1968vs; (THF) 1970vs; ($C_6H_6/CHCl_3$ [3/7]) 1970vs cm^{-1}. ^1H NMR (C_6H_6-d_6/$CHCl_3$-*d* [3/7], 24 °C) δ 7.3 (m, 30H); 5.8 (s, 2H); 1.9 (s, 6H). Due to the low solubility in organic solvents, it was not possible to obtain a ^{13}C spectrum. Mass spectrum, *m/e* (rel. intensity). M^+ 837(0.8); $(M-\text{pyr})^+$ 743(0.4); $(M-AsPh_3)^+$ 531(23.8); $(M-[CO, AsPh_3])^+$ 503(100); $(M-[CO, AsPh_3, \text{pyr}])^+$ 408 (24.9).

2,5-Dimethylpyrrolyldicarbonyliridium(I) dimer (4)

A solution of 700 mg Li-2,5-dimethylpyrrolide (700 mg, 6.9 m*M*, in 25 ml THF) was added dropwise to a suspension of $[IrCl(CO)_3]_n$ (400 mg, 1.28 m*M*, in 20 ml THF) at r.t. and under N_2 with vigorously stirring. The addition was stopped after ca. 1 h, at which time all of the $[IrCl(CO)_3]_n$ had dissolved and a light-red solution formed. The solvent was then evaporated under oil pump vacuum at ca. 30 °C and the red-orange, sticky residue was extracted with ca. 50 ml of diethyl ether. The extract was passed through a Schlenk frit, and the red filtrate was concentrated at r.t. until precipitation occurred. The remaining solvent was removed as completely as possible with a syringe and the solid was washed with 10 ml of n-hexane to yield 500 mg (57%) of a pale yellow, air-sensitive powder, soluble in THF, acetone, slightly soluble in benzene and chloroform, and insoluble in n-hexane, m.p. 135 °C (dec.). *Note*: In some other runs the product separated as an orange oil. In order to convert it into a powder, it was kept for several hours under vacuum and then treated with a 1 : 1 mixture of n-hexane and dichloromethane. Anal. Found: C, 28.66; H, 3.34; N, 3.95. $C_{16}H_{16}N_2O_4Ir_2$ calc.: C, 28.05; H, 2.33; N, 4.09%. IR: ν(CO) (KBr): 1978vs, 2045vs; (THF) 1945vs, 2021s; (acetone/n-hexane [2/10]) 1950vs, 2025s; (acetone) 1946vs, 2020vs; ($CHCl_3$) 1982vs, 2059vs cm^{-1}. ^1H NMR (acetone-d_6, 100.0 atom% D, 25 °C): δ 2.1 (s, 6); 5.3 (s, 2); ($CHCl_3$-*d*, 25 °C) δ 2.1 (s, 6); 5.69, 5.72 (s, 2). Mass spectrum: *m/e* (rel. intensity) M^+ 684(3.0); $(M-[\text{Ir, 2CO}])^+$ 436(100); $(M-[\text{Ir, 3CO}]-{}^+$ 406(36.7); $(M-[\text{Ir, 4CO}])^+$ 380(32.0); $(M-[\text{Ir, 2CO, pyr}])^+$ 343; $(M-[\text{Ir, 3CO, pyr}])^+$ 313(66.2).

trans-2,5-Dimethylpyrrolocarbonylbis(triphenylphosphine)iridium(I) (5)

To a solution of **4** (50 mg, 0.07 mM) in 20 ml diethyl ether and 10 ml THF was added 1.5 g (5.7 mM) of PPh_3, and the mixture was stirred at r.t. for about 2 h. The solvents were evaporated off and the residue was washed with 4 × 20 ml of n-hexane, yielding 100 mg (85%) of a yellow, slightly air sensitive powder, m.p. 255 ° C (dec.), soluble in THF, slightly soluble in diethyl ether and chloroform, and insoluble in n-hexane. Anal. Found: C, 57.13; H, 4.63; N, 1.60. $C_{43}H_{38}NOP_2Ir$ calc.: C, 61.56; H, 4.53; N, 1.67%. IR: ν(CO) (KBr): 1956vs; (THF) 1960vs cm^{-1}. ^1H NMR: ($CHCl_3$-d, 24°C) δ 1.47 (s, 6H); 5.25 (s, 2H); 7.2 (s, 30H). ^{31}P (THF/acetone-d_6 [7/3], 22°C) δ value rel. to H_3PO_4 (85%) as an external standard: δ 26.3(s). Mass spectrum: m/e (rel. intensity) M^+ 839(43.8); $(M-\text{pyr})^+$ 745(15.1); $(M-[\text{CO, pyr}])^+$ 715(36.6); $(M-\text{PPh}_3)^+$ 577(100); $(M-[\text{CO, PPh}_3])^+$ 549(22.9).

The method of synthesis for *trans*-2,5-dimethylpyrrolocarbonylbis(triphenylarsine)iridium(I) (**6**) was similar to that of **5**: 50 mg of **4** (0.07 mM); 1.5 g $AsPh_3$ (4.9 mM). Reaction time 20 h at r.t. Yield: 70 mg (54%), greenish-yellow, air sensitive powder, m.p. 230 ° C (dec), soluble in THF, moderately soluble in benzene, unsoluble in n-hexane and diethyl ether. Anal. Found: C, 48.78; H, 4.16; N, 1.60. $C_{43}H_{38}NOAs_2Ir$ calc.: C, 55.72; H, 4.10; N, 1.51%. IR: ν(CO) (KBr) 1952vs; (THF) 1959vs cm^{-1}. ^1H NMR: (C_6H_6-d_6; 24°C) δ 2.1 (s, 6H); 6.1 (s, 2H); 7.2 (s, br, 30 H). Mass spectrum: m/e (rel. intensity), M^+ 927(7.5); $(M-\text{AsPh}_3)^+$ 621(100); $(M-[\text{AsPh}_3, \text{CO, pyr}])^+$ 498(47.2); $(M-[\text{Ph, AsPh}_3, \text{CO, pyr}])^+$ 419(96.2).

X-Ray crystal structure determination

Table 1 contains details of the crystal data collection and refinement parameters. Specimens of **1** and **2** suitable for data collection were obtained by recrystallization in 2/1 ether/hexanes at −10 ° C. Preliminary photographic characterization showed that both possessed $2/m$ Laue symmetry. Systematic absences in the diffraction data uniquely assigned space group $P2_1/c$ to **1** and indicated the choices of $P2_1$ or $P2_1/m$ for **2**. For **2**, the centrosymmetric alternative was initially chosen by positioning the mirror plane perpendicular to the P–Rh–P axis. It became quickly apparent that the planes of the pyrrole and phenyl rings were not compatible with m-site symmetry and further processing was confined to the noncentrosymmetric alternative. The computationally stable and chemically reasonable final structure confirms the validity of this decision. The unit-cell parameters were obtained from the least-squares fit of 25 high-angle reflections chosen to contain Friedel-related sets to inspect optical and diffractometer alignment.

Both structures were solved by heavy-atom methods and completed by subsequent difference Fourier syntheses. All nonhydrogen atoms were treated anisotropically.The phenyl rings in **2** were constrained to regular hexagonal geometry. All the hydrogen atoms in both structures were found, but only those attached to C(3) and C(4) in **1** were refined; the remainder were incorporated in idealized locations and updated but not refined. The correct enantiomorph for **2** was confirmed unambiguously by refinement of a multiplicative term for $\Delta f''$.

The atomic coordinates for **1** and **2** are given in Tables 2 and 3, respectively, and selected bond distances and angles in Tables 4 and 5. ORTEP structures of **1** and **2** are shown in Figs. 1 and 2, respectively. The P3 and SHELXTL program libraries were used in all computations (Nicolet Corp., Madison, WI).

(Continued on p. 229)

Table 1

Crystal data for **1** and **2**

	1	**2**
Formula	$C_{16}H_{16}N_2O_4Rh_2$	$C_{43}H_{48}NOP_2Rh$
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1$
Crystal size (mm)	0.23×0.31×0.33	0.30×0.38×0.38
Crystal color	orange	yellow
a (Å)	8.639(2)	9.891(3)
b (Å)	7.734(1)	12.014(3)
c (Å)	13.436(3)	15.167(5)
β (°)	103.09(2)	93.42(3)
V (Å^3)	874.4(3)	1799(1)
Z	2	2
D_{calc} (g cm^{-3})	1.922	1.402
Abs. coeff. (cm^{-1})	18.4	5.4
Diffractometer	Nicolet R3m/μ	
Radiation	Mo-K_α (λ 0.71073 Å)	
Monochromator	graphite crystal	
Temp. (°C)	24	
Scan technique	omega	Wyckoff
Scan speed (° min^{-1})	variable, 4–20	variable, 6–20
2θ scan limits, (°)	4–60	4–55
Data collected	$\pm h$, $+k$, $+l$	$\pm h$, $+k$, $+l$
Data read	2821	4493
Independent data	2543	4330
Independent data observed	2046 with $\|F_0\| \geqslant 4\sigma(F_0)$	3919 with $\|F_0\| \geqslant 4\sigma(F_0)$
R(int.) (%)	2.62	1.43
Std. rflns.	3 std./197 rflns. (< 2% var.)	3 std/197 rflns. (1% var.)
g, $w^{-1} = \sigma^2(F_0) + g \cdot F_0^2$	0.001	0.001
R_F (%)	2.54	2.95
R_{wF} (%)	3.04	3.18
GOF	0.955	0.923
Δ/σ	0.015	0.086
Max. contour (e$^-$/Å^3)	0.60	0.47
NO/NV	17.3	10.8

Table 2

Atomic coordinates (×10^4) and isotropic thermal parameters (Å^2 ×10^3) for **1**

Atom	x	y	z	U [a]
Rh	2299.9(2)	1947.4(2)	559.1(1)	37.9(1)
N	789(2)	857(3)	−717(1)	35.1(6)
O(8)	4504(4)	3535(5)	2362(2)	81(1)
O(9)	3825(3)	3950(4)	−844(2)	76(1)
C(2)	1063(3)	−707(3)	−1134(2)	43(1)
C(3)	−325(4)	−1331(4)	−1729(2)	51(1)
C(4)	−1521(4)	−58(4)	−1700(2)	47(1)
C(5)	−753(3)	1301(4)	−1095(2)	38(1)
C(6)	2714(4)	−1447(5)	−961(3)	60(1)
C(7)	−1356(4)	3064(4)	−968(3)	54(1)
C(8)	3674(4)	2911(4)	1678(2)	52(1)
C(9)	3228(4)	3217(4)	−315(2)	48(1)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3

Atomic coordinates ($\times 10^4$) and isotropic thermal parameters (Å$^2 \times 10^3$) for **2**

Atom	x	y	z	U [a]
Rh	6092.1(2)	2500	2653.5(2)	29.0(1)
P(1)	6019.2(9)	623.6(8)	2251.2(6)	29.2(2)
P(2)	6173.7(9)	4396.1(9)	2993.6(6)	29.2(3)
N	7897(3)	2675(3)	2026(2)	33(1)
O	3824(4)	2165(3)	3811(3)	81(2)
C(1)	9178(3)	2572(5)	2447(3)	42(1)
C(2)	10111(4)	2762(4)	1833(4)	57(2)
C(3)	9400(5)	2969(4)	1012(4)	57(2)
C(4)	8056(4)	2915(4)	1154(3)	41(1)
C(5)	9370(6)	2267(4)	3389(4)	64(2)
C(6)	6865(5)	3089(5)	521(3)	55(2)
C(7)	4652(5)	2299(3)	3330(3)	48(1)
C(11)	6652(3)	−139(2)	3948(2)	50(1)
C(12)	7188	−879	4587	62(2)
C(13)	7948	−1792	4337	65(2)
C(14)	8173	−1965	3448	70(2)
C(15)	7638	−1225	2809	51(1)
C(16)	6877	−313	3060	34(1)
C(21)	8128(2)	355(3)	1131(1)	37(1)
C(22)	8696	86	338	44(1)
C(23)	7867	−267	−385	48(1)
C(24)	6471	−351	−315	50(1)
C(25)	5904	−83	478	41(1)
C(26)	6732	270	1201	32(1)
C(31)	4144(2)	−1142(2)	2192(2)	41(1)
C(32)	2862	−1607	2024	53(2)
C(33)	1763	−926	1772	60(2)
C(34)	1947	220	1689	69(2)
C(35)	3229	684	1857	53(2)
C(36)	4328	3	2109	34(1)
C(41)	8172(2)	5267(2)	1939(2)	41(1)
C(42)	8649	5961	1289	56(2)
C(43)	7784	6736	866	60(2)
C(44)	6442	6818	1094	57(2)
C(45)	5964	6124	1744	42(1)
C(46)	6830	5348	2167	34(1)
C(51)	4531(2)	5982(2)	3781(2)	4591)
C(52)	3298	6493	3929	60(2)
C(53)	2100	6079	3522	63(2)
C(54)	2134	5155	2967	58(2)
C(55)	3367	4645	2819	43(1)
C(56)	4565	5058	3226	36(1)
C(61)	8480(3)	5104(3)	4079(2)	51(1)
C(62)	9196	5211	4895	65(2)
C(63)	8620	4848	5662	63(2)
C(64)	7328	4379	5613	63(2)
C(65)	6611	4272	4797	53(2)
C(66)	7187	4635	4030	34(1)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4

Selected bond distances (Å) and angles (°) for $[(CO)_2RhNC_6H_8]_2$

Rh–N	2.084(2)	N–C(2)	1.376(3)
Rh–C(3a)	2.613(3)	C(2)–C(3)	1.369(4)
Rh–C(4a)	2.324(3)	C(3)–C(4)	1.434(5)
Rh–C(8)	1.848(3)	C(4)–C(5)	1.400(4)
Rh–C(9)	1.847(3)	C(5)–N	1.358(3)
C(8)–O(8)	1.137(4)	C(2)–C(6)	1.505(4)
C(9)–O(9)	1.122(5)	C(5)–C(7)	1.483(4)
N–Rh–C(8)	178.8(1)	Rh–C(8)–O(8)	178.6(3)
N–Rh–C(9)	88.5(1)	Rh–C(9)–O(9)	177.9(3)
C(8)–Rh–C(9)	90.6(1)	Rh–N–C(2)	123.9(2)
C(4a)–Rh–N	93.8(1)	Rh–N–C(5)	125.7(2)
C(4a)–Rh–C(8)	86.9(1)	N–C(2)–C(3)	109.8(2)
C(4a)–Rh–C(9)	170.2(1)	C(2)–C(3)–C(4)	106.4(3)
C(3a)–Rh–N	92.8(1)	C(3)–C(4)–C(5)	106.4(2)
C(3a)–Rh–C(8)	88.3(1)	C(4)–C(5)–N	108.8(2)
C(3a)–Rh–C(9)	156.4(1)	C(2)–N–C(5)	108.4(2)

Table 5

Selected bond distances (Å) and angles (°) for $(Ph_3P)_2Rh(CO)(NC_6H_8)$

Rh–P(1)	2.335(1)	C(1)–C(2)	1.368(7)
Rh–P(2)	2.336(1)	C(2)–C(3)	1.415(8)
Rh–C(7)	1.821(5)	C(3)–C(4)	1.362(6)
Rh–N	2.083(3)	C(4)–N	1.372(5)
C(7)–O	1.140(7)	C(1)–C(5)	1.477(7)
N–C(1)	1.389(4)	C(4)–C(6)	1.490(6)
P(1)–Rh–N	89.5(1)	Rh–N–C(1)	124.3(2)
P(1)–Rh–P(2)	177.6(0)	Rh–N–C(4)	127.7(2)
P(1)–Rh–C(7)	90.3(1)	N–C(1)–C(2)	107.8(4)
N–Rh–P(2)	89.0(1)	C(1)–C(2)–C(3)	107.9(4)
N–Rh–C(7)	172.5(2)	C(2)–C(3)–C(4)	106.9(4)
P(2)–Rh–C(7)	91.3(1)	C(3)–C(4)–N	109.4(4)
Rh–C(7)–O	174.4(4)	C(1)–N–C(4)	107.9(3)

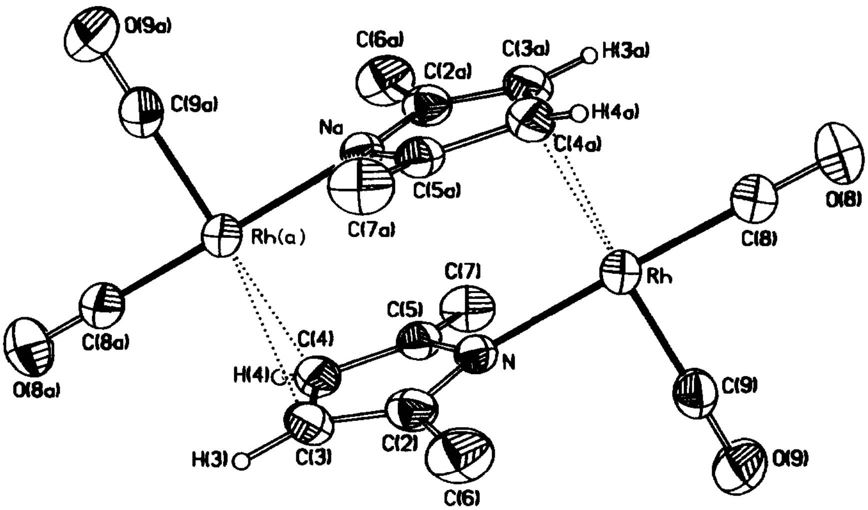


Fig. 1. ORTEP drawing of compound **1**.

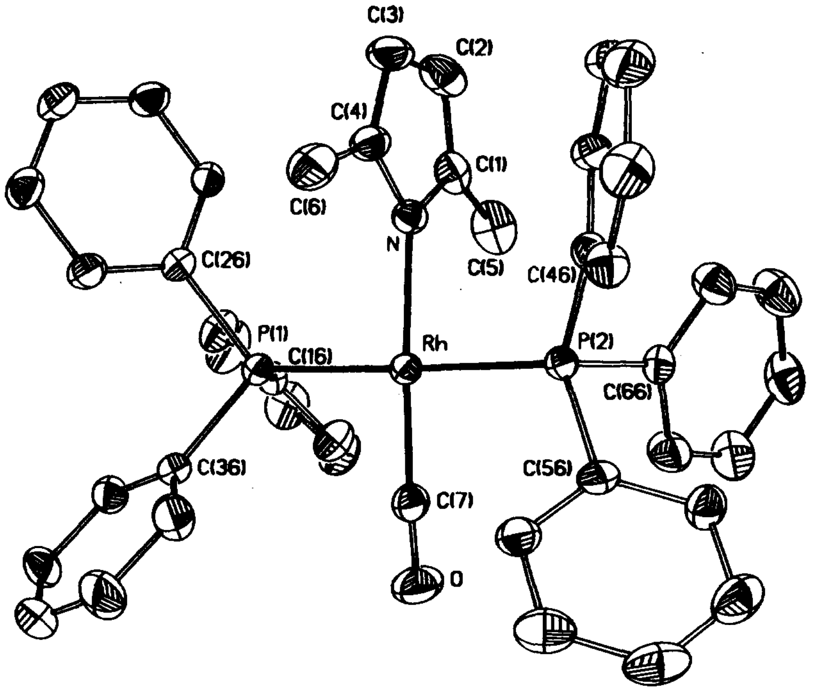
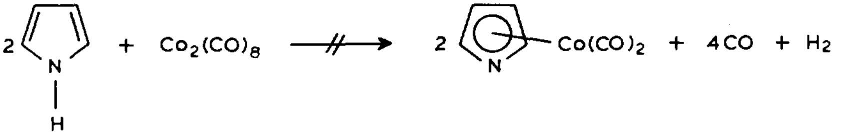


Fig. 2. ORTEP drawing of compound 2.

Results

Cyclopentadienylmetal carbonyls of the type η^5-$(C_5H_5)M(CO)_2$ (M = Co, Rh, Ir) are readily prepared by the reaction of cyclopentadiene with $Co_2(CO)_8$ [16] or by the reaction of the cyclopentadienide anion with $[RhCl(CO)_2]_2$ [17] or $[IrCl(CO)_3]_n$ [18]. Our attempts to synthesize the corresponding pyrrolyl complexes of cobalt, (η^5-pyr)$Co(CO)_2$, using pyrrole and the 2,5- and 3,4-dimethylpyrroles by heating or irradiating these pyrroles in the presence of $Co_2(CO)_8$ in THF or n-hexane were unsuccessful (eq. 1).



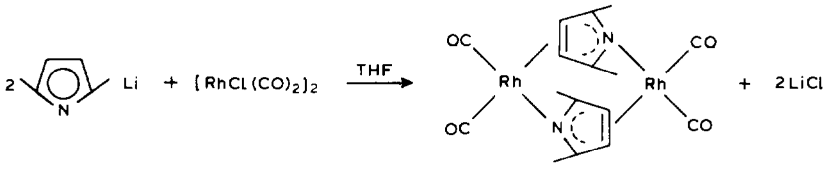
(1)

The IR spectrum of the initial reaction mixture showed the expected ν(CO) bands of $Co_2(CO)_8$ at 1855 and 2020 cm^{-1}, but these bands persisted, indicating that no reaction had taken place even after several days, initially at room temperature and then at elevated temperatures. We were also not able to prepare $CoI(CO)_4$ by the published method [19] using iodine and $Co_2(CO)_8$ as reactants and hexadecane as a solvent. Somewhat as expected, at the high reaction temperatures reported we always obtained high yields of the stable tetramer $Co_4(CO)_{12}$. We were, however, able to prepare $CoI(CO)_4$ by the modified method described by Palyi et al. [26]

involving use of $Co_2(CO)_8$ and I_2 in THF at −78 °C. The product was not isolated, but the dark brown solution was treated with lithium-2,5-dimethylpyrrolide at −70 °C. After a reaction time of 15 min the solution turned green, and subsequent evaporation of the solvent yielded a sticky green material. The IR spectrum in the ν(CO) region showed only one broad band at ca. 1970 cm^{-1}. No further characterization of this product was attempted.

In another approach we mixed $(\eta^3\text{-}C_3H_5)Co(CO)_3$ with the lithium salt of 2,5-dimethylpyrrole in THF/hexane, expecting the formation of allyllithium and $(\eta^5\text{-}2,5\text{-}(CH_3)_2C_4H_2N)Co(CO)_2$. Even after several hours at 50 °C, there was no IR-spectroscopic evidence for the formation of the expected products.

For the attempted synthesis of compounds of the type $(\eta^5\text{-pyr})Rh(CO)_2$ we chose as starting materials $[RhCl(CO)_2]_2$ and the Lipyr salts. The reaction of Li-2,5-dimethylpyrrolide with $[RhCl(CO)_2]_2$ in THF afforded a yellow powder, which had an IR spectrum in the CO stretch region with values of ν(CO) at 1991 and 2050 cm^{-1} (benzene) that are very similar to the known values for $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ (1987, 2051 cm^{-1}) [18]. However, its mass spectrum, with a molecular fragment of $M^+ = 506$, suggests the formation of a dimer. Since elemental analyses, IR, and NMR data give no help in deciding between a monomeric and dimeric structure, crystals of the compound were grown for X-ray study. The structure was found to be a dimer, formed by the reaction represented by eq. 2:



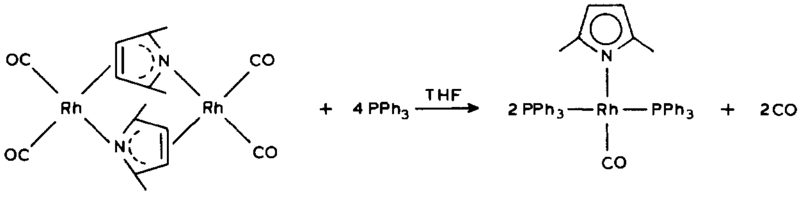
(1)

(2)

Compound **1** is an air-sensitive yellow powder, stable at 0 °C for several weeks and decomposing at about 140 °C. It dissolves in several organic solvents at r.t. to give red solutions. The red color of the solution darkens on standing at r.t. for a few hours. This color change from a yellow solid to a deep red solution does not appear to be due to decomposition, since concentration of the dark red solutions regenerates the original yellow solid in high yield. Also the mass spectrum of such a red benzene solution showed the rhodium compound to be identical with that of freshly prepared solid **1**. In view of these results, we are reluctant to assume that red solutions of **1** contain the desired monomeric $(\eta^5\text{-}2,5\text{-}(CH_3)_2C_4H_2N)Rh(CO)_2$.

Further characterization of **1** was achieved by NMR spectroscopy. ^1H NMR spectra obtained using $CHCl_3\text{-}d$, $C_6H_6\text{-}d_6$ or acetone-d_6 indicate the correct proton ratio of 2/6. However, the ring ($\sim\delta$ 5.8 ppm) and the methyl protons ($\sim\delta$ 2.1 ppm) seem not to be magnetically equal and give rise to at least three signals (Fig. 1). If the environment of these protons were ideally symmetrical, one would expect only two doublets for each group of protons (coupling with ^{103}Rh, spin 1/2). Since the X-ray structure shows that the pyrrole ring in the molecule displays an unusual coordination type, it may be that because of considerable ring distortion the methyl and the ring protons do not have magnetically equal environments. Also, the ^{13}C spectrum in $CHCl_3\text{-}d$ exhibits more signals than expected, but a tentative assignment of these signals is possible.

Since the synthesis of the intended (η^5-pyr)Rh(CO)$_2$ was not accomplished, it was thought that perhaps compound **1** might react with a nucleophile L to form the desired monomer (η^5-pyr)Rh(CO)L. Surprisingly, the reaction of **1** with either PPh$_3$, or even with the extremely weak nucleophile AsPh$_3$, proceeds very vigorously at room temperature and is complete within a few minutes. The products are yellow air stable powders which decompose at temperatures of about 200 °C. Their IR spectra in the CO stretching region have only one sharp band for PPh$_3$ (1987 cm^{-1}, THF) and for AsPh$_3$ (1970 cm^{-1}, THF). The uncomplicated ^{1}H NMR spectra with proton ratio of 30/6/2 indicate coordination of either two PPh$_3$ or two AsPh$_3$ groups. Also molecular fragments in the mass spectra of both products confirm the presence of only one CO group. However, the bonding mode of the pyrrole ring was again disclosed only by X-ray structure analysis, which was performed for the PPh$_3$ product **2**. This means the reactions proceed according to eq. 3:



(3)

(1) (2)

Rhodium complexes are known to differ from the corresponding cobalt and iridium complexes in their chemical reactivity (e.g., substitution ability at the metal centers) [12,20]. Since we were unable to prepare (η^5-pyr)M(CO)$_2$ (M = Co, Rh), it seemed worthwhile to try the same reactions with an iridium carbonyl. The method used for synthesis of (η^5-C$_5$H$_5$)Ir(CO)$_2$ [12,18] was tried but with pyrrole instead of cyclopentadiene. The reaction between Li-2,5-dimethylpyrrolide and [IrCl(CO)$_3$]$_n$ seemed to proceed in the same way as that described for the synthesis of compound **1**. In both cases, the products separate from a diethyl ether solution and are isolated as relatively pure powders. Since [IrCl(CO)$_3$]$_n$ is almost insoluble in organic solvents, the reaction requires ca. 15 h for completion if the starting materials are employed in 1/1 ratio. Unfortunately, with a more prolonged reaction time the Ir product **4** tends to decompose. Therefore, an excess of the pyrrole anion was used, and this led to completion of the reaction after ca. 1 h. The poor C, H and N analyses for compound **4** (see Experimental) might therefore result from the presence of unreacted pyrrolide anion, which precipitates out from the diethyl ether solution in the presence of **4**.

The Ir compound **4**, like the Rh compound **1**, is an air sensitive yellow solid, which decomposes at 135 °C and forms light red solutions. Its IR spectrum (KBr) shows two ν(CO) bands at 1978 and 2045 cm^{-1}, comparable with the values of **1** (1976, 2041 cm^{-1}). The ^{1}H NMR spectrum in acetone-d_6 shows two singlets and in CHCl$_3$-d a singlet (for CH$_3$) and a doublet (for ring). In both cases the proton ratio is 6/2 and additional signals found in the spectrum of **1** are absent (Fig. 3). The solubility of **4** in organic solvents is considerably lower than that of **1**, a fact which prevented the recording of a ^{13}C NMR spectrum. Interestingly, the mass spectrum exhibits a molecular peak $M^+ = 684$, which by analogy to **1**, corresponds to a dimeric structure.

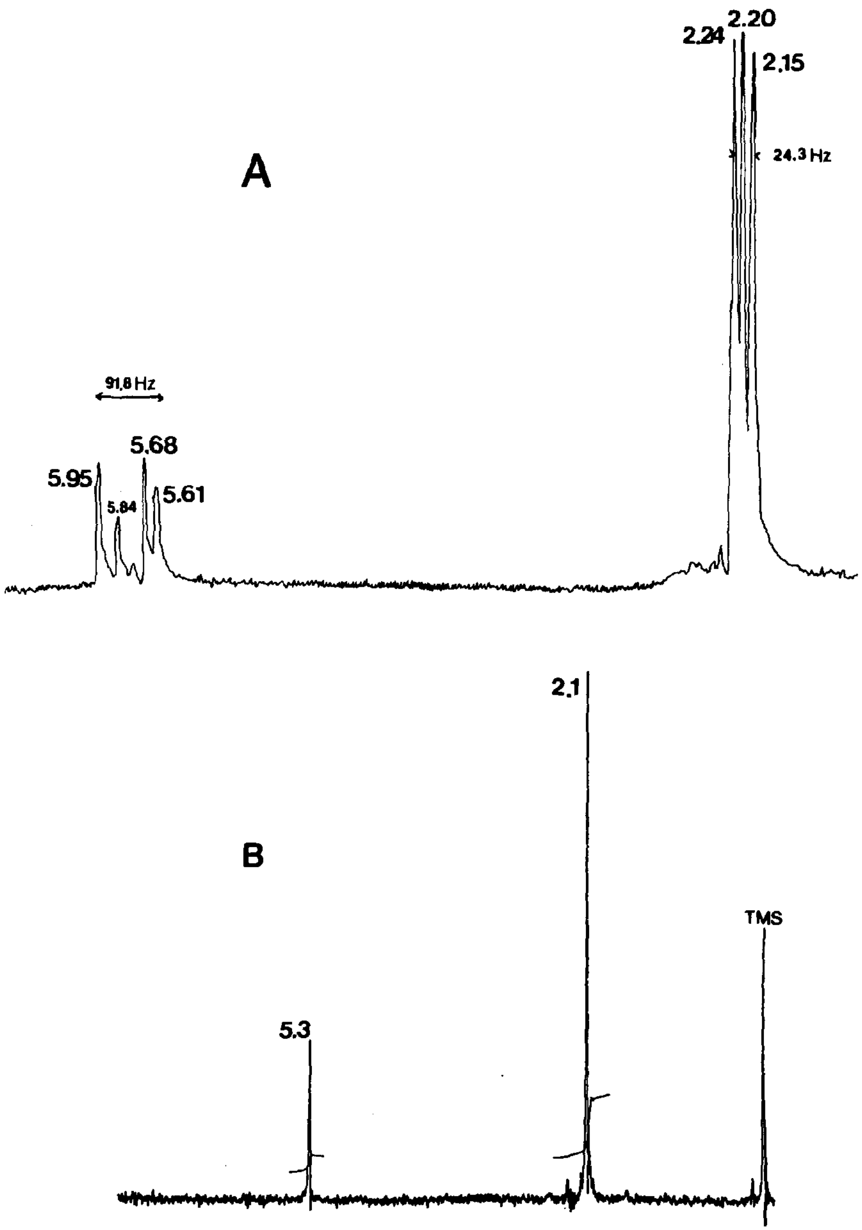


Fig. 3. ^{1}H NMR spectrum (A) of compound **1** in CHCl$_3$-d and (B) of compound **4** in acetone-d_6 (100% atom D) at r.t. The proton ratio methyl/ring is in both cases 6/2. pyr = 2,5-dimethylpyrrole.

The reaction of **4** with either PPh$_3$ or AsPh$_3$ is slower than that of **1**; in particular the immediate vigorous CO formation observed in the case of **1** does not occur with **4**. This is in accord with the fact that ligand substitution reactions of Ir are slower than corresponding reactions of Rh compounds [12,20]. Although the rates of reaction differ, the products of reaction of **4** are close analogous to the Rh complexes **2** and **3**. The IR spectra of the Ir products, PPh_3 (**5**) and $AsPh_3$ (**6**), exhibit only one band in the ν(CO) region. The ^1H NMR and mass spectra, as well as elemental analyses, indicate the coordination of either two PPh_3 or two $AsPh_3$ groups along with one 2,5-dimethylpyrrole and one CO group per Ir. The ^{31}P NMR spectrum of **5** shows one sharp singlet at 26.3 ppm. This is in accord with ^{31}P NMR investigations on *trans* square-planar complexes of iridium, which, in contrast to the *cis* isomers, exhibit one signal [27]. Similarly, our square-planar rhodium complex shows one clear doublet at δ 26.3 and 27.1 ppm (due to the coupling with ^{103}Rh) and verifies the *trans* arrangement of the PPh_3 ligands. In view of these results it appears that **5** and **6** have structures analogous to **2** and **3**. Unfortunately, **5** and **6** have low solubilities and so ^{13}C spectra were not obtained.

It seems reasonable to suggest that the structure of **4** is similar to that of **1**. However, since the ^1H NMR spectrum of **4** exhibits two sharp singlets without any additional signals shown by **1**, it appears that the Ir dimer **4** suffers much less molecular distortion in solution than does the corresponding Rh dimer **1**.

Reactions between $[RhCl(CO)_2]_2$ and the anions of pyrrole and of 3,4-dimethylpyrrole were also investigated. Unfortunately, these reactions did not yield identifiable products. In both cases the products were black sticky masses, which when extracted with n-hexane became powders. Their IR spectra were unhelpful, showing only one broad band in the ν(CO) region at about 1950 cm^{-1}. Mass spectra were unsatisfactory, exhibiting a very high number of fragments with generally low abundance, and the desired molecular peaks were not detectable. It appeared that the reactions gave a complex mixture of products, and no further attempts were made to investigate them.

Other studies included reactions between $[RhCl(CO)_2]_2$ and the anions of 2,5-dimethylarsole and 2,5-dimethylphosphole. After reduction of the arsole with MeLi in THF the product was treated with $[RhCl(CO)_2]_2$ as described for preparation of complex **1**. The IR spectrum of the brownish sticky product had two relatively sharp ν(CO) bands at 1991 and 2061 cm^{-1} and a broad band at about 1960 cm^{-1}. Attempts to convert the product into a powder failed, so work on the arsole compounds was discontinued. Finally 2,5-dimethylphosphole was reduced with K and the product treated with $[RhCl(CO)_2]_2$ in THF. The black powder obtained had an IR spectrum with only one broad band in the ν(CO) region at about 1970 cm^{-1}. No further characterization was attempted.

Discussion

It is known that pyrrole (C_4H_5N) and its substituted derivatives (e.g. 2,5- and 3,4-dimethylpyrrole) [9,21] form σ-N bonded as well as π-bonded metal complexes. The π-bonded complexes are analogous to η^5-cyclopentadienylmetal complexes. Although there is a delicate balance between σ and π bonding of heterocycles to metals, the formation of heteroatom–metal σ bonds are generally preferred because the unbonded electron pairs on the heteroatom have lower ionization energies relative to the electrons in the π system [8]. However, organometallic compounds of heterocycles in which the heterocyclic ligand is complexed to metal centers by utilization of both the σ and η^2-π bonding modes of the same ring, with formation of a highly distorted metal–olefin moiety, have not to our knowledge been previously reported [22]. We have observed what is believed to be the first example of this, through the syntheses and characterization of σ and η^2-π bonded pyrrole in dimeric rhodium and iridium carbonyls.

The X-ray structure determination of 2,5-dimethylpyrrolyldicarbonylrhodium(I) shows it has a dimeric structure (**1**) in which each pyrrole ring acts as both σ and π donor (Fig. 1). In order to maintain the preferred 16-electron count for square planar Rh^I complexes, it is suggested the lone pair of electrons on the N atom form a σ bond with one Rh metal center, while a π interaction occurs between the second Rh metal center and the C(3) and C(4) ring atoms. Such bonding is possible given an allyl-ene anion formulation for the bridging ligand, and there is evidence [21] that slippage towards such as formulation is favored in pyrrolyl metal complexes. It should be noted that this is an η^2 type π bonding, not the usual η^5 type found for π-bonded cyclopentadienyl to metals. Furthermore this Rh complex is a 16-electron system, not the 18-electron system present in $(\eta^5\text{-}C_5H_5)Rh(CO)_2$. Thus, the bonding in this Rh dimer results in a distortion of the coordinated pyrrole ring, with a consequent loss of symmetry. This reduction of symmetry is also indicated by the NMR spectra, which have more signals (Fig. 3) than would be expected for an ideal symmetrical coordination.

The corresponding iridium carbonyl **4** has a less complicated ^1H NMR spectrum, indicating a higher symmetry of the coordinated heterocycles. Unfortunately, we were unable to grow suitable crystals for determination of the X-ray structure of **4**, but we believed it to be analogous to that of the rhodium dimer **1**. This assumption is supported by mass spectra data, and by the fact that it reacts with PPh_3 and $AsPh_3$ to form compounds of the type $Ir(pyr)COL_2$ which are similar to the corresponding Rh complexes.

The X-ray structure of the monomeric rhodium derivative **2** shows it to be a square planar Rh^I complex, with the two PPh_3 groups in *trans* positions and the remaining *trans* positions occupied by CO and by the σ-bonded pyrrolide ion. This is in accord with the ^{31}P NMR solution spectrum, which shows presence of the *trans* isomer. This four-coordinate Rh^I is a 16-electron system, as is its dimeric precursor **1**. That the parent compound **1** readily reacts with PPh_3 and $AsPh_3$ is in accord with the known rapid associative ligand substitution reactions of 16-electron Rh^I complexes [20].

The reason why in all of these compounds σ-bonding is preferred to η^5-coordination of the pyrrollide ligand remains an open question. We believed that the 2,5-dimethylpyrrole, with its two methyl groups *ortho* to the ring N atom would provide steric hindrance to σ-N coordination, thus favoring η^5-coordination. Not only does σ-N coordination occur, but in the dimer the same pyrrole ring also acts as an η^2-π donor and leads to a highly distorted structure rather than the more symmetrical structure in which the ring is η^5 coordinated. Preference for a π-olefinic metal interaction is known to occur when the 5-membered heterocyclic ring contains a heteroatom more electronegative than C. This slippage towards an η^2 geometry arises from the interaction of the metal d_{yz} and d_{xy} orbitals with the π-heterocyclic ring [23]. There is also a precedent in the literature for an $\eta^5 \rightarrow \eta^1$ rearrangement of the η^5-pyrrolyl ligand. Azoferrocene $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_4H_4N)]$ is known to undergo a facile reaction with π-acidic ligands L to afford η^1-*N*-pyrrolyl complexes of the type $(\eta^5\text{-}C_5H_5)FeL_2(\eta^1\text{-}NC_4H_4)$ [24]. This is similar to the $\eta^5 \rightarrow \eta^1$ rearrangements known for reactions of certain cyclopentadienyl metal complexes [25].

Pyrroles form η^5-bonded complexes with the $Mn(CO)_3$ moiety, and we find that

(η^5-C_4H_4N)Mn(CO)$_3$ undergoes CO substitution reactions faster by orders of magnitude than those of the cyclopentadienyl analogue (η^5-C_5H_5)Mn(CO)$_3$. Our goal was to prepare the compounds (η^5-C_4H_4N)M(CO)$_2$ (where M = Co, Rh, Ir) and to compare the rates of their CO substitutions with the known rates for corresponding (η^5-C_5H_5)M(CO)$_2$ compounds. Why the desired compounds were not obtained remains a mystery and we note only that for heterocyclic ligands there is a delicate balance between the energetics of the bonding modes. It is not even understood why 2,5-dimethylpyrrole gives stable Rh and Ir products, whereas pyrrole and 3,4-dimethylpyrrole do not. It goes without saying that much more work is needed if these behaviors are to be understood.

Supplementary Material Available

Structure factor tables, anisotropic thermal parameters and hydrogen atom coordinates may be obtained from Arnold L. Rheingold at the University of Delaware.

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