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THE FORMATION AND MOLECULAR STRUCTURE OF (η^5-NITROCYCLOPENTADIENYL)DICARBONYLRHODIUM

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Summary

A reaction between sodium or lithium nitrocyclopentadienide and dichlorotetracarbonyldirhodium produces (η^5-nitrocyclopentadienyl)dicarbonylrhodium in 22—30% yield, the first η-nitrocyclopentadienyl-transition metal compound to be synthesized directly from nitrocyclopentadienide anion. The product has been characterized by spectroscopic and by X-ray diffraction techniques, the latter representing the first such structural determination for a nitrocyclopentadienylmetal compound. Red crystals of the title compound are triclinic, $P\bar{1}$, with $a = 6.247(4)$, $b = 6.484(4)$, $c = 11.311(6)$ Å, $\alpha = 76.79(5)$, $\beta = 79.40(5)$, $\gamma = 72.95(5)°$, and $D_c = 2.12$ g cm^{-3} for $Z = 2$. Least-squares refinement gave a final conventional R value of 0.056 for 1438 independent observed reflections. The nitrocyclopentadienyl ligand is significantly nonplanar.

Introduction

Even though sodium nitrocyclopentadienide (I) was the first cyclopentadienyl-metal compound to be synthesized in a pure state [1], nitrocyclopentadienyl-metal compounds have seldom been described in the literature. In the transition metal series, η-nitrocyclopentadienyl derivatives are presently limited to nitroferrocene (III) [2—4] and nitrocymantrene (IV) [5]. Both III and IV have been synthesized only by multi-step routes from the parent compounds ferrocene and cymantrene, respectively, and overall yields of III and IV were very low. Earlier attempts to prepare η-nitrocyclopentadienyl derivatives of iron from I or from nitrocyclopentadiene proved to be unsuccessful [3,4,6,7].

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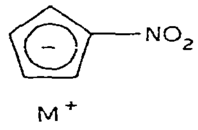
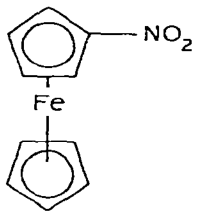
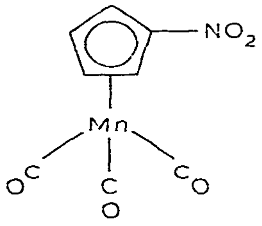


(I, M = Na ;
II, M = Li)



(III)



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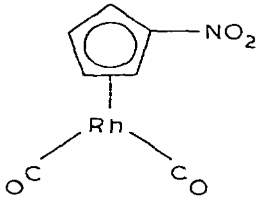

(V)

Experimental

A. Synthetic procedure

All synthetic operations were conducted using Schlenk tube techniques under an atmosphere of dry, oxygen-free nitrogen. $[Rh(CO)_2Cl]_2$ and sodium nitrocyclopentadienide [1] were prepared according to literature methods. Lithium nitrocyclopentadienide was prepared from lithium cyclopentadienide and ethyl nitrate in THF solution (12 hours, 25°C). The THF was partially removed and the salt was washed with ethyl ether and dried. Hexane was distilled under argon from calcium hydride before use, whereas THF and ethyl ether were dried over sodium and distilled under argon from sodium-benzophenone. IR, NMR and mass spectra were obtained on Beckmann IR-10, Varian A-60 and Perkin-Elmer-Hitachi RMU-6L instruments, respectively. Microanalyses were performed by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts, Amherst, Massachusetts.

Reaction of sodium nitrocyclopentadienide and dichlorotetracarbonyldirhodium. A solution of sodium nitrocyclopentadienide (1.71 g, 12.8 mmol) and dichlorotetracarbonyldirhodium (1.25 g, 3.2 mmol) in 100 ml of anhydrous THF was stirred at 25°C for 12 hours under nitrogen. The solvent was then removed under reduced pressure, and the resulting orange residue was dissolved in 20 ml of anhydrous ethyl ether. Activated silica gel (1—2 g) was added, the solvent removed under reduced pressure, and the coated silica gel was then added to a silica gel column packed dry under nitrogen. Elution with hexane brought down a faint yellow band which was not collected. Continued elution with 1 : 1 to 2 : 1 ether/hexane removed the major orange band. Evaporation of the solvent afforded 0.52 g (30%) of an orange solid. An analytical sample was obtained by vacuum sublimation (25°C, 10^{-2} mm Hg), producing red crystals of V suitable for X-ray analysis, m.p. 62—63°C. (Found: C, 30.96; H, 1.46. $C_7H_4NO_4Rh$ calcd.: C, 31.25; H, 1.50%).

TABLE 1
CRYSTAL DATA

Mol. formula	$RhO_4NC_7H_4$
Mol. weight	269.0
Linear abs. coeff (cm^{-1})	19.52
Calc. density (g cm^{-3})	2.12
Max. crystal dimensions (mm)	0.10 × 0.28 × 0.36
Space group	$P\bar{1}$
Molecules/unit cell	2
Cell constants [a] a, (Å)	6.247 (4)
b, (Å)	6.484 (4)
c, (Å)	11.311 (6)
α, (°)	76.79 (5)
β, (°)	79.40 (5)
γ, (°)	72.95 (5)
Cell volume (Å^3)	423

[a] Mo K_α radiation, λ 0.71069 Å. Ambient temperature of 23 ± 1°C.

B. Crystal structure determination

Single crystals of V were mounted and sealed in thin-walled glass capillaries. Final lattice parameters, as determined from a least-squares refinement of the angular settings of 15 reflections centered accurately on an Enraf-Nonius CAD-4 diffractometer, are given in Table 1. Data were collected using graphite crystal monochromated radiation and the ω—2θ scan technique in a manner similar to that previously described [8].

Measurement of one independent quadrant of data out to $2\theta = 50°$ led to the collection of 1438 independent observed reflections [$I > 3\sigma(I)$]. The intensities were corrected for Lorentz and polarization effects, but not for absorption (μ 19.5 cm^{-1}).

The position of the rhodium atom was revealed after inspection of a Patterson synthesis map, and the subsequent difference Fourier afforded the coordinates of the remaining non-hydrogen atoms.

The full-matrix least-squares refinement was carried out using the Busing and Levy program ORFLS [9]. The function $w(|F_0| - |F_c|)^2$ was minimized. No correction was made for extinction. Neutral atom scattering factors were from the compilations of Cromer and Waber [10] for Rh, O, N, and C, and those for hydrogen were taken from ref. 11. The scattering for rhodium was corrected for the real and imaginary components of anomalous dispersion with the table of Cromer and Liberman [12]. Isotropic refinement of the non-hydrogen atoms yielded $R_1 = \Sigma(|F_0| - |F_c|)/\Sigma|F_0| = 0.113$. Conversion to anisotropic temperature factors, positioning of the hydrogens in calculated positions, and further refinement led to final values of $R_1 = 0.056$ and $R_2 = [\Sigma w(|F_0| - |F_c|)^2/\Sigma|F_0|^2]^{1/2} = 0.065$. The weighting scheme was based on unit weights for all but the most intense reflections ($F_c > 50$), which were assigned $\sigma = 5.0$. The final value of the esd of an observation of unit weight was 1.31. The final positional and thermal parameters are given in Table 2 *.

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TABLE 2

FINAL FRACTIONAL COORDINATES AND THERMAL PARAMETERS[a] FOR $(C_5H_4NO_2)Rh(CO)_2$

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Rh	0.1485(1)	0.2475(1)	0.18002(6)	0.0262(2)	0.0171(2)	0.00712(7)	−0.0090(1)	−0.00376(8)	−0.00146(7)
O(1)	0.245(2)	0.139(1)	−0.0704(8)	0.068(4)	0.041(3)	0.0097(8)	−0.020(2)	−0.006(1)	−0.005(1)
O(2)	0.323(2)	0.644(1)	0.0762(8)	0.065(4)	0.29(2)	0.014(1)	−0.027(3)	0.006(3)	−0.004(1)
O(3)	0.356(1)	−0.382(1)	0.3472(8)	0.051(3)	0.018(2)	0.017(1)	−0.006(2)	−0.011(1)	−0.007(1)
O(4)	0.541(1)	−0.188(1)	0.4008(7)	0.030(2)	0.033(2)	0.0135(8)	−0.010(1)	−0.010(1)	−0.001(1)
N	0.374(1)	−0.209(1)	0.3660(7)	0.031(2)	0.018(2)	0.0094(7)	−0.006(2)	−0.006(1)	−0.0022(9)
C(1)	0.204(2)	0.179(2)	0.0248(9)	0.040(4)	0.024(3)	0.0079(9)	−0.012(2)	−0.005(1)	−0.003(1)
C(2)	0.258(2)	0.490(2)	0.114(1)	0.040(4)	0.025(3)	0.0089(9)	−0.012(3)	0.000(1)	−0.003(1)
C(3)	0.181(1)	−0.021(1)	0.3507(7)	0.025(2)	0.016(2)	0.0071(7)	−0.008(2)	−0.003(1)	−0.002(1)
C(4)	−0.008(1)	−0.012(2)	0.2987(9)	0.026(3)	0.025(3)	0.0088(9)	−0.014(2)	−0.014(2)	−0.001(1)
C(5)	−0.165(2)	0.192(2)	0.310(1)	0.025(3)	0.029(3)	0.011(1)	−0.009(2)	−0.003(1)	0.001(1)
C(6)	−0.060(2)	0.312(2)	0.3591(9)	0.034(3)	0.023(3)	0.0092(9)	−0.003(2)	0.000(1)	−0.003(1)
C(7)	0.158(2)	0.180(1)	0.3854(8)	0.034(3)	0.021(2)	0.0065(7)	−0.011(2)	−0.002(1)	−0.003(1)
H(1)	−0.033	−0.126	0.261	4.5					
H(2)	−0.322	0.242	0.286	4.5					
H(3)	−0.129	00.463	0.376	4.5					
H(4)	0.270	0.223	0.419	4.5					

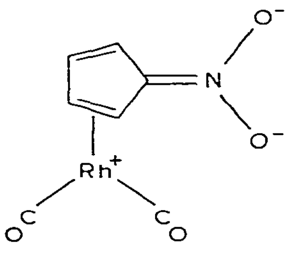
[a] Anistropic temperature factors are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Results and discussion

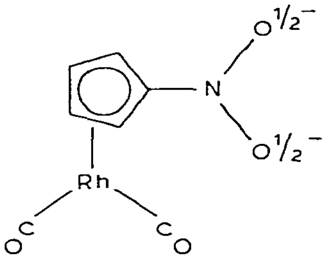
We report the first direct synthesis of an η-nitrocyclopentadienyl-transition metal compound starting with the nitrocyclopentadienide anion and a transition metal halide. In a typical experiment, a molar excess of I and $[Rh(CO)_2Cl]_2$ were stirred in THF solution for 12 hours at room temperature. Removal of the solvent and chromatography of the product afforded a yellow-orange solid, which on vacuum sublimation produced red crystals of (η^5-nitrocyclopentadienyl)dicarbonylrhodium (V) in 30% yield. Lithium nitrocyclopentadienide (II), prepared from lithium cyclopentadienide and ethyl nitrate in THF at 25°C, reacts with $[Rh(CO)_2Cl]_2$ in an analogous manner to form V in 22% yield.

The IR spectrum (KBr) of V exhibits strong intensity bands at 1500 and 1320 cm^{-1} which are characteristic [13] for aromatic -NO_2 asymmetric and symmetric stretching frequencies, respectively. Metal carbonyl bands (2060 and 1990 cm^{-1}) as well as bands characteristic for a mono-substituted cyclopentadienyl ring are also present. The proton NMR spectrum of V contains two apparent triplets (A_2B_2) of equal intensity at δ 5.70 and 6.28 ppm, assignable [14] to the $H_{3,4}$ and $H_{2,5}$ protons, respectively. The higher field resonance shows additional splitting, due possibly to unequal spin—spin interaction with the ^{103}Rh nucleus [9]. Both the $H_{2,5}$ and $H_{3,4}$ protons in V are strongly deshielded by the nitro substituent with respect to protons in the parent compound (η^5-C_5H_5)$Rh(CO)_2$ (δ 5.44 ppm, a result which has been observed for other nitrocyclopentadienyl-metal compounds [5,15]. The mass spectrum of V exhibits major peaks at *m/e* 269 [50, M^+], 241 [70, $(M - CO)^+$], 213 [50, $(M - 2\ CO)^+$], 183 [100, $(M - 2\ CO - NO)^+$], 167 [35, $(M - 2\ CO - NO_2)^+$], 103 [20, Rh^+] and 30 [5, NO^+]. Strong molecular ions as well as the fragmentation ions represented by peaks at *m/e* 183, 167 and 30 are especially characteristic of aromatic nitro compounds [13].

The molecular structure and atom numbering scheme of V are shown in Figure 1. Bond distances and angles are given in Table 3. One of the most important questions concerning the title compound pertains to the relative contribution of resonance structures A and B.



(A)



(B)

Localization in substituted cyclopentadienyl rhodium(I) compounds has previously been implied [16] and, indeed, one might expect the nitro group to stabilize resonance form A. Scrutiny of Table 3 shows that the C—C bond lengths

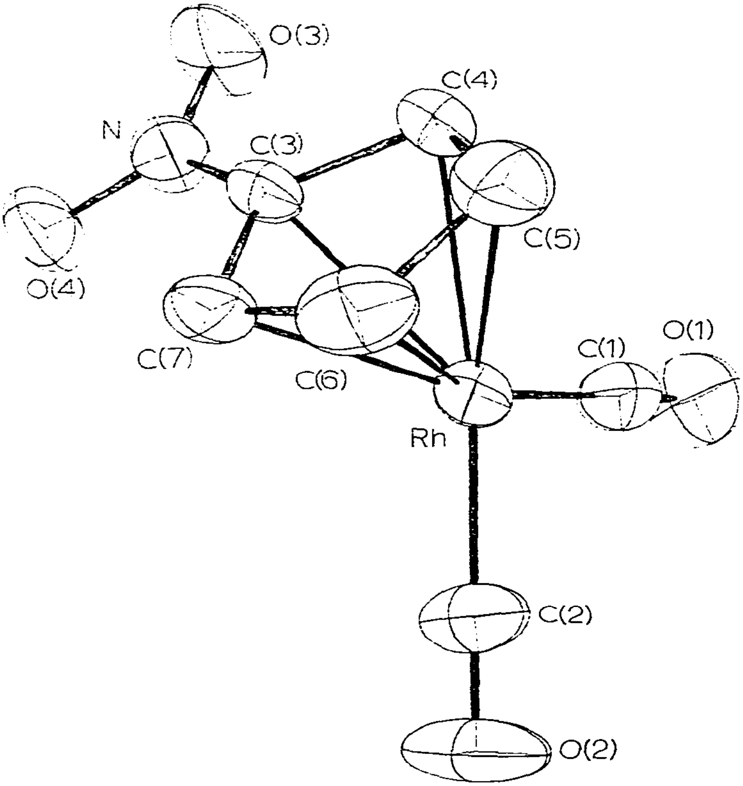
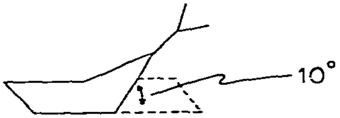


Fig. 1. Molecular structure for (η^5-$C_5H_4NO_2$)Rh(CO)$_2$.

are not significantly different from the average, and the N—C length, 1.44(1) Å, while slightly below the norm for a single bond implies a large contribution from B.

The $C_5H_4NO_2^-$ ligand is only planar to 0.10 Å (Table 4). C(3) resides 0.06 Å out of the plane of C(4), C(5), C(6), and C(7) which in turn show a maximum deviation of only 0.02 Å. On the other hand, C(3), N, O(3), and O(4) are planar to within 0.012 Å. The two planar units make an angle of 10° with each other (C). These results may best be explained by a significant contribution from A.



(C)

Since angles may be more easily deformed than bond lengths, we conclude that the accuracy of the C—C lengths is not sufficient to show localization. Stated differently, the extent of localization in V is not great.

The Rh—C(cyclopentadienyl) distances which range from 2.244(9) to 2.29(1) and average 2.270 Å, compare closely to the average values of 2.24 Å

TABLE 3

BOND LENGTHS (Å) AND ANGELS (°) FOR (η^5-$C_5H_4NO_2$)Rh(CO)$_2$

Bond Lengths:			
Rh—C(1)	1.86(1)	Rh—C(2)	1.85(1)
Rh—C(3)	2.280(8)	Rh—C(4)	2.244(9)
Rh—C(5)	2.29(1)	Rh—C(6)	2.25(1)
Rh—C(7)	2.272(9)		
C(1)—O(1)	1.13(1)	C(2)—O(2)	1.15(1)
C(3)—C(4)	1.39(1)	C(4)—C(5)	1.42(1)
C(5)—C(6)	1.40(2)	C(6)—C(7)	1.42(1)
C(3)—C(7)	1.40(1)	C(3)—N	1.44(1)
N—O(3)	1.22(1)	N—O(4)	1.23(1)
Bond Angles:			
C(1)—Rh—C(2)	88.5(4)	O(1)—C(1)—Rh	177.2(9)
O(2)—C(2)—Rh	177.7(9)		
C(7)—C(3)—C(4)	110.3(8)	C(3)—C(4)—C(5)	107.2(8)
C(4)—C(5)—C(6)	107.1(8)	C(5)—C(6)—C(7)	109.4(8)
C(6)—C(7)—C(3)	105.6(8)	C(7)—C(3)—N	124.8(7)
C(4)—C(3)—N	124.8(7)	C(3)—N—O(3)	117.3(7)
C(3)—N—O(4)	118.5(7)	O(3)—N—O(4)	124.2(8)

and 2.26 Å found in [(C_5H_5)Rh(CO)]$_3$ [17] and $Rh_2(C_5H_5)_2(CO)_3$ [18], respectively. The Rh—C(carbonyl) distances, at 1.85(1) and 1.86(1) Å agree well with previously determined values of 1.87 [18] and 1.86 Å [19].

The cell-packing is illustrated in Figure 2. There are no abnormally close intermolecular contacts.

TABLE 4

BEST LEAST-SQUARES PLANES TREATMENT OF ($C_5H_4NO_2$)

(i) Plane defined by C(4), C(5), C(6), C(7)

$0.3442X + 0.2186Y - 0.9155Z + 2.6825 = 0$

Deviations of atoms from plane (Å)

C(4)	0.011	C(5)	−0.018
C(6)	0.018	C(7)	−0.011
C(3)	−0.058		

(ii) Plane defined by C(3), N, O(3), O(4)

$0.2881X + 0.0682Y - 0.09552Z + 3.0907 = 0$

Deviations from plane (Å)

C(3)	−0.003	N	0.012
O(3)	−0.004	O(4)	−0.004

Angle between (i) and (ii) is 9.52°

(iii) Plane defined by C(3), C(4), C(5), C(6), C(7)

$0.3564X + 0.2035Y - 0.9119Z + 2.6994 = 0$

Deviations from plane (Å)

C(3)	−0.024	C(4)	0.030
C(5)	−0.025	C(6)	0.011
C(7)	0.008	N	−0.096
Rh	1.925		

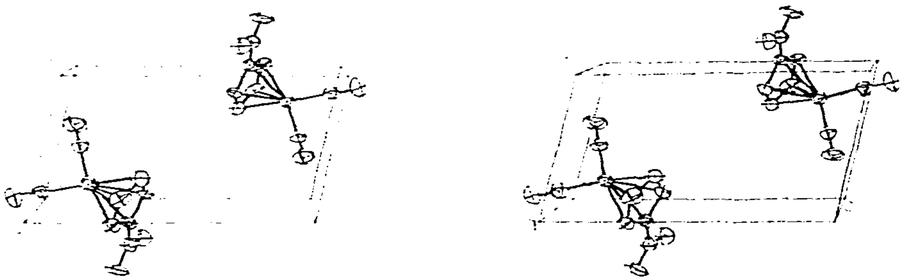


Fig. 2. Stereoscopic view of the unit cell packing for (η^5-$C_5H_4NO_2$)Rh(CO)$_2$.

Acknowledgements

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