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Effects of changes in the ligands on the skeleton and the catalytic activity of some new rhodium complexes with pyrazolato moieties

Herbert Schumann, Holger Hemling and Vadde Ravindar

Institut für Anorganische und Analytische Chemie, Technische Universität Berlin, D-10623 Berlin (Germany)

Yacoub Badrieh and Jochanan Blum

Department of Organic Chemistry, The Hebrew University, Jerusalem 91904 (Israel)

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Abstract

Whereas the reaction of $[Rh(CO)_2(\mu\text{-pz})]_2$ (where pz is either a pyrazolato or 3,5-dimethylpyrazolato group) with 3-(diphenylphosphino)benzoic acid and (2-formylphenyl)diphenylphosphine gives the dinuclearic complexes $[Rh(CO)(Ph_2P\text{-}3\text{-}C_6H_4COOH)(\mu\text{-pz})]_2$ (**1** and **2**) and $[Rh(CO)(Ph_2P\text{-}2\text{-}C_6H_4CHO)(\mu\text{-pz})]_2$ (**5** and **6**) respectively, 2-(diphenylphosphino)benzoic acid gives the monorhodium compounds $Rh(CO)(H\text{-pz})(Ph_2P\text{-}2\text{-}C_6H_4COO)$ (**3** and **4**). The structures of $Rh(CO)(N{=}CHCH{=}CHNH)(Ph_2P\text{-}2\text{-}C_6H_4COO)$ (**3**) and $[Rh(CO)(Ph_2P\text{-}2\text{-}C_6H_4CHO)(\mu\text{-}NCMe{=}CHCMe{=}N)]_2$ (**6**) have been determined by X-ray diffraction analyses. Both, the monorhodium and the dirhodium complexes catalyse the hydroformylation of acyclic and cyclic olefins at 120°C and at CO and H_2 pressures of 28 atm. At 70–90°C the dinuclear complexes with 3-(diphenylphosphino)benzoic acid moieties are substantially more active than the monorhodium compounds.

Key words: Rhodium; Phosphine; Hydroformylation; X-ray diffraction

1. Introduction

Pyrazolato-monometal and pyrazolato-dimetal complexes have attracted substantial interest in the past two decades [1–3]. Some of these complexes were found to possess high catalytic activity for various hydrogen transfer processes and to be of considerable value in synthesis (see for example refs. 4–6). Recently [7], we have shown that some rhodium-pyrazolato complexes promote the transformation of mono-aryl alkynes to poly(arylacetylenes) in a unique stereoselective manner, and that their catalytic activity is strongly dependent on minor structural features. We now report the syntheses of some new pyrazole-containing rhodium complexes, their structure determination and their utilization as alkene hydroformylation catalysts.

2. Results and discussion

The reaction of an alkali pyrazolate, di-μ-chlorobis[(1,2,5,6-η)-1,5-cyclooctadiene]dirhodium, CO and tertiary phosphine, described by Usón *et al.* [8] as a general route to pyrazolato bridged dirhodium complexes, was found to be applicable to **1**, **2**, **5** and **6**:

$$[(COD)Rh(\mu\text{-Cl})]_2 \xrightarrow[-2Cl^-]{2pz^-} [(COD)Rh(\mu\text{-pz})]_2 \xrightarrow[-2COD]{4CO} [(CO)_2Rh(\mu\text{-pz})]_2 \xrightarrow[-2CO]{2PR_3} [(PR_3)Rh(CO)(\mu\text{-pz})]_2 \qquad (1)$$

Dirhodium complexes were obtained when the tertiary phosphine was either 3-(diphenylphosphino)benzoic acid or (2-formylphenyl)diphenylphosphine. However,

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Correspondence to: Professor H. Schumann or Professor J. Blum.

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when the phosphine moiety contained a carboxyl group in the *ortho* position, as in 2-(diphenylphosphino)benzoic acid, the monorhodium complexes **3** and **4** were formed instead. The process is assumed to involve proton transfer from the carboxyl moiety to the pyrazole group through rhodium-assisted oxidative addition–reductive elimination processes.

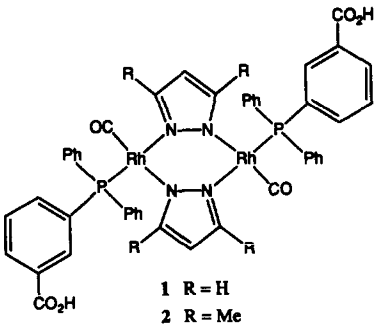
The interaction of $[(CO)_2Rh(\mu\text{-pz})]_2$ with 4-(diphenylphosphino)benzoic acid was also associated with hydrogen transfer, through which, however, polymeric rhodium complexes were produced.

While the dirhodium complexes **1**, **2**, **5** and **6** showed IR bands characteristic for aromatic acid and aldehyde carbonyl at 1710 cm^{-1}, 1716 cm^{-1}, 1680 cm^{-1} and 1685 cm^{-1} respectively, the corresponding carbonyl absorptions of **3** and **4** appeared at 1602 cm^{-1} and 1595 cm^{-1}.

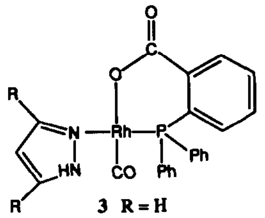
As a representative of the monorhodium complexes, **3** was subjected to X-ray diffraction analysis (Fig. 1). The data given in Tables 1–3 indicate that the complex is square planar, with the rhodium atom coordinated to the pyrazole nitrogen (2.119(7) Å), to the carbonyl function (1.798(9) Å), to the phosphorus (2.209(2) Å) and to the carboxylate oxygen (Rh–O(2), 2.048(6) Å) (compare, for example, refs. 9–11). The L–Rh–L angles between these coordinating ligands vary between 84.6 and 95.9°, and their sum is 360.0(3)°. The maximum deviation out of the plane formed by the coordinating ligands does not exceed 0.042 Å above (pz) or 0.050 Å below (Rh) the plane. Atoms Rh, P(2), C(7), C(8), C(9) and O(2) form an envelope-shaped six-membered ring and atoms O(2), C(7), C(8) and C(9) are coplanar with the conjugated aromatic ring. The sp^2 orbitals at C(7) and C(8) transfer the planarity; hence the P(2)–C(7)–C(8)–C(10), C(9)–C(8)–C(7)–C(13) and O(2)–C(7)–C(8)–C(9) torsion angles are 179.1°, 179.3° and −0.4(13)° respectively. While the sp^2 centres of C(9) and P(2) are coplanar with the benzene ring, atoms O(2) and Rh are out of the plane by 0.56(4) Å and 1.28(4) Å, respectively. The pyrazole ring is planar

TABLE 1. Crystal data and details of structure determination for **3** and **6**

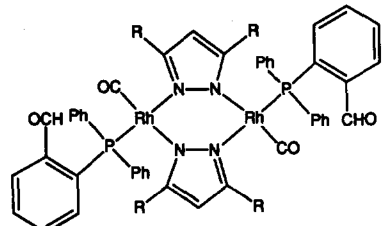
	3	6
Formula	$C_{23}H_{18}N_2O_3PRh$	$C_{48}H_{44}N_4O_4P_2Rh_2\cdot 2(C_2H_5)_2O$
Molecular weight	504.3	1082.8
Space group	*C*2/*c*	*C*2/*c*
Crystal system	Monoclinic	Monoclinic
Crystal dimensions (mm × mm × mm)	0.15 × 0.15 × 0.25	0.2 × 0.15 × 0.2
a (Å)	17.635(7)	18.356(4)
b (Å)	10.918(2)	28.129(5)
c (Å)	21.848(5)	11.425(3)
β (°)	93.57(3)	113.33(2)
V (Å³)	4199(2)	5417(2)
ρ_{calc} ($g\,cm^{-3}$)	1.586	1.328
F(000)	2032	2204
Linear absorption coefficient (cm^{-1})	9.0	7.0
Radiation	Mo Kα (λ = 0.71069 Å)	Mo Kα (λ = 0.71069 Å)
Temperature (K)	165	165
Range (°)	$1 \leq 2\theta \leq 46$	$1 \leq 2\theta \leq 48$
hkl boundaries	0 → 19, 0 → 12, −24 → 24	−21 → 21, 0 → 32, 0 → 13
Scan technique	ω–2θ	ω–2θ
Scan time variable (s)	Maximum 45	Maximum 45
Scan angle (°)	$0.57 + 0.35 \tan\theta$	$0.67 + 0.35 \tan\theta$
Aperture (mm)	2	2
Number of reflections measured	3637	4308
Number of unique reflections	3517 (R_{int} = 0.019)	4081 (R_{int} = 0.0199)
Number of observed reflections with $F_o > 4\sigma(F_o)$	3258	3663
Residual electron density (eÅ³)		
Maximum	0.974	1.216
Minimum	−0.768	−0.474
Absorption (DIFABS)		
Maximum	1.409	1.066
Minimum	0.889	0.869
Number of refined parameters	292	303
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.0330	0.0373



1 R = H
2 R = Me



3 R = H
4 R = Me



5 R = H
6 R = Me

(maximum deviation by N(1), 0.09(10) Å). The observed N(2)–H distance is 0.73(5) Å.

TABLE 2. Refined positional and isotropic thermal parameters for **3** with estimated standard deviations in parentheses

Atom	x	y	z	B_{eq} (Å^2)
Rh(1)	0.64283(4)	0.36557(6)	0.14769(3)	1.56
P(2)	0.4035(1)	0.2103(1)	0.4077(1)	1.76
C(1)	0.4534(2)	0.2652(4)	0.4775(2)	1.86
C(2)	0.4171(3)	0.3500(4)	0.5127(2)	2.65
C(3)	0.4529(3)	0.3952(5)	0.5662(2)	2.94
C(4)	0.5256(3)	0.3574(5)	0.5841(2)	2.41
C(5)	0.5626(3)	0.2739(5)	0.5493(2)	2.55
C(6)	0.5267(2)	0.2277(4)	0.4958(2)	2.41
C(7)	0.4759(2)	0.1306(4)	0.3661(2)	1.87
C(8)	0.5260(2)	0.1955(4)	0.3322(2)	1.88
C(9)	0.5258(2)	0.3340(4)	0.3254(2)	1.97
O(1)	0.5886(2)	0.3815(3)	0.3169(1)	2.67
O(2)	0.4652(2)	0.3952(3)	0.3265(1)	2.61
C(10)	0.5810(3)	0.1319(5)	0.3017(2)	2.96
C(11)	0.5849(3)	0.0060(5)	0.3047(3)	4.01
C(12)	0.5357(3)	−0.0580(5)	0.3390(3)	4.02
C(13)	0.4815(3)	0.0034(4)	0.3698(2)	2.92
C(14)	0.3407(2)	0.0895(4)	0.4310(2)	2.20
C(15)	0.2881(3)	0.0410(4)	0.3874(2)	2.43
C(16)	0.2391(3)	−0.0507(4)	0.4030(3)	2.78
C(17)	0.2412(3)	−0.0934(5)	0.4630(3)	3.86
C(18)	0.2937(3)	−0.0465(5)	0.5059(2)	3.96
C(19)	0.3439(3)	0.0445(4)	0.4905(2)	2.58
C(20)	0.2630(3)	0.3388(4)	0.3758(2)	2.38
O(3)	0.2028(2)	0.3185(3)	0.3909(2)	3.16
N(1)	0.3292(2)	0.5276(3)	0.3033(2)	2.36
N(2)	0.3634(2)	0.5608(4)	0.2537(2)	2.80
C(21)	0.3449(3)	0.6741(4)	0.2359(2)	3.63
C(22)	0.2967(3)	0.7191(5)	0.2770(2)	4.22
C(23)	0.2872(3)	0.6249(5)	0.3187(2)	3.30

As an example of the pyrazolato-bridged dirhodium complexes, **6** was examined by X-ray diffraction. A suitable crystal was obtained as a temperature-sensitive disolvate by low temperature crystallization from Et$_2$O (Fig. 2). (At room temperature the crystals collapse to a solvent-free powder.) The data listed in Tables 1, 4 and 5 indicate that **6** exists as a hinged dinuclear complex with an *anti* configuration. The complete structure could be generated by a symmetry operation $[-x, y, \frac{1}{2}(-z)]$ on half of the molecule. The phosphorus, the carbonyl carbon and two nitrogen atoms (one of each pz ring) form a square planar geometry around one rhodium nucleus, as demonstrated by the sum of the interligand angles of 361.3(3)°. The angle between the two wings of the hinged configuration is 88.1° and is similar to the angle in related dirhodium complexes (see for example ref. 12). The two pyrazolato bridges and the two rhodium atoms (Rh(1)–N(2)–N(1′)–Rh(1′)–N(2′)–N(1)) form a six-membered boat structure with the four nitrogen atoms forming the base. As a consequence the Rh–Rh distance is rather long (3.479(1) Å) compared with those in other related dirhodium species (see for example ref. 13) and excludes metal–metal interaction. The pyrazole rings are almost planar (maximum deviation at N(1), 0.006(13) Å). There is no significant twisting of the sp^2 orbitals of C(20) and C(23), although a small distortion of 0.035 Å at the methylated carbon atoms C(21) and C(24) has been observed. The interplanar angle between the two pyrazole moieties is 79.0(2)°, pointing away from the |Rh–Rh| vector.

The crystal packing of **6** provides free space which is occupied by uncoordinated Et$_2$O molecules. The loca-

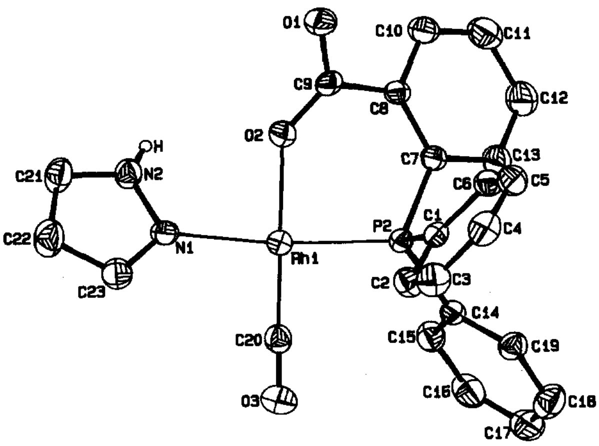


Fig. 1. Molecular structure (ORTEP) of **3**.

tion of the ether atoms C(26)–C(27)–O(3)–C(28)–C(29) is defined by the position of C(29) which lies close to a twofold axis. Thus the solvate molecules are distributed in such a manner that 50% lie to the right and 50% to the left of C(29). The unit cell consists of four dirhodium moieties with eight solvent molecules.

All six rhodium complexes **1**–**6** proved to catalyse hydroformylation of the model acyclic and cyclic olefins 1-dodecene (**7**) and cyclohexene (**8**). Thus, at 120°C

TABLE 3. Selected bond lengths and angles for **3** with estimated standard deviations in parentheses

	Bond length (Å)		Bond length (Å)
Rh–P(2)	2.209(2)	Rh–O(2)	2.048(6)
Rh–N(1)	2.119(7)	Rh–C(20)	1.798(9)
C(1)–C(2)	1.385(6)	C(11)–C(12)	1.373(7)
C(1)–C(6)	1.392(6)	C(12)–C(13)	1.377(7)
C(1)–P(2)	1.815(4)	C(14)–C(15)	1.393(6)
C(2)–C(3)	1.385(7)	C(14)–C(19)	1.388(6)
C(3)–C(4)	1.380(7)	C(14)–P(2)	1.816(4)
C(4)–C(5)	1.379(7)	C(15)–C(16)	1.379(7)
C(5)–C(6)	1.387(6)	C(16)–C(17)	1.388(8)
C(7)–C(8)	1.384(6)	C(17)–C(18)	1.375(8)
C(7)–C(13)	1.394(6)	C(18)–C(19)	1.386(7)
C(7)–P(2)	1.831(4)	C(20)–O(3)	1.153(5)
C(8)–C(9)	1.519(6)	C(21)–C(22)	1.364(7)
C(8)–C(10)	1.396(6)	C(21)–N(2)	1.331(6)
C(9)–O(1)	1.247(5)	C(22)–C(23)	1.392(7)
C(9)–O(2)	1.262(5)	C(23)–N(1)	1.350(6)
C(10)–C(11)	1.377(7)	N(1)–N(2)	1.324(5)
N(2)–H	0.73(5)		
	Bond angle (°)		Bond angle (°)
O(2)–Rh–N(1)	89.6(3)	O(2)–Rh–P(2)	87.9(2)
O(2)–Rh–C(20)	179.3(3)	N(1)–Rh–P(2)	170.6(2)
N(1)–Rh–C(20)	95.9(3)	C(20)–Rh–P(2)	92.1(3)
C(1)–P(2)–C(7)	104.9(2)	O(1)–C(9)–O(2)	122.9(4)
C(1)–P(2)–C(14)	106.0(2)	C(8)–C(10)–C(11)	120.6(4)
C(7)–P(2)–C(14)	104.4(2)	C(10)–C(11)–C(12)	120.1(5)
P(2)–C(1)–C(2)	118.1(3)	C(11)–C(12)–C(13)	120.1(5)
P(2)–C(1)–C(6)	122.5(3)	C(7)–C(13)–C(12)	120.4(5)
C(2)–C(1)–C(6)	119.4(4)	P(2)–C(14)–C(15)	118.5(3)
C(1)–C(2)–C(3)	120.3(4)	P(2)–C(14)–C(19)	122.1(3)
C(2)–C(3)–C(4)	120.0(5)	C(15)–C(14)–C(19)	119.5(4)
C(3)–C(4)–C(5)	120.3(4)	C(14)–C(15)–C(16)	120.5(4)
C(4)–C(5)–C(6)	119.8(4)	C(15)–C(16)–C(17)	119.8(5)
C(1)–C(6)–C(5)	120.2(4)	C(16)–C(17)–C(18)	119.8(5)
P(2)–C(7)–C(8)	120.7(3)	C(17)–C(18)–C(19)	120.9(5)
P(2)–C(7)–C(13)	119.6(3)	C(14)–C(19)–C(18)	119.5(5)
C(8)–C(7)–C(3)	119.7(4)	N(2)–N(1)–C(23)	105.9(4)
C(7)–C(8)–C(9)	124.4(4)	N(1)–N(2)–C(21)	112.2(4)
C(7)–C(8)–C(10)	119.1(4)	N(2)–C(21)–C(22)	107.1(4)
C(9)–C(8)–C(10)	116.5(4)	C(21)–C(22)–C(23)	105.7(4)
C(8)–C(9)–O(1)	115.6(4)	N(1)–C(23)–C(22)	109.0(4)
C(8)–C(9)–O(2)	121.4(4)		

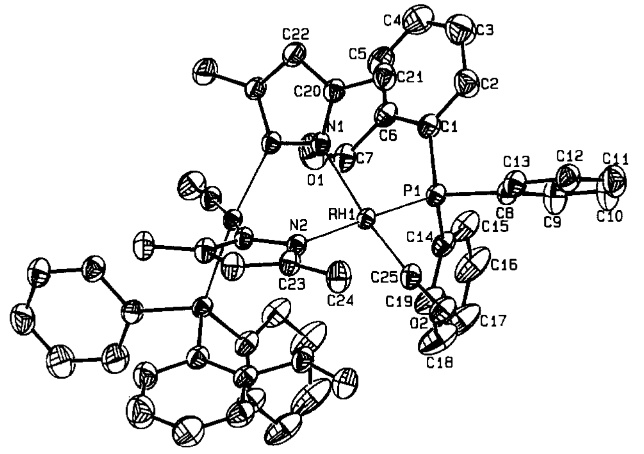


Fig. 2. Molecular structure (ORTEP) of **6**. (The solvate molecules are not shown.)

TABLE 4. Refined positional and isotropic thermal parameters for **6** with estimated standard deviations in parentheses [a]

Atom	x	y	z	B_{eq} (Å^2)
Rh(1)	0.59771(2)	0.67666(1)	0.36115(3)	1.90
P(1)	0.1783(1)	0.12950(4)	0.3057(1)	2.14
N(1)	0.0624(2)	0.2182(1)	0.1949(3)	2.13
N(2)	0.0119(2)	0.2138(1)	0.4010(3)	2.07
O(1)	−0.0089(2)	0.1054(1)	−0.0700(3)	3.51
O(2)	0.1763(2)	0.1342(1)	0.6186(3)	3.90
O(3)	0.1330(14)	0.4503(9)	0.0303(2)	18.20
C(1)	0.1847(2)	0.1434(1)	0.1529(4)	2.67
C(2)	0.2531(3)	0.1612(2)	0.1514(4)	3.43
C(3)	0.2590(3)	0.1744(2)	0.0365(5)	5.17
C(4)	0.1954(3)	0.1676(2)	−0.0768(5)	5.19
C(5)	0.1255(3)	0.1497(2)	−0.0777(4)	3.62
C(6)	0.1195(2)	0.1376(1)	0.0364(4)	2.81
C(7)	0.0429(2)	0.1184(1)	0.0298(4)	2.61
C(8)	0.2824(2)	0.1282(2)	0.4154(4)	2.82
C(9)	0.3327(3)	0.0907(2)	0.4163(5)	4.13
C(10)	0.4131(3)	0.0930(2)	0.4947(6)	5.40
C(11)	0.4435(3)	0.1313(2)	0.5742(5)	4.13
C(12)	0.3944(3)	0.1677(2)	0.5763(4)	3.10
C(13)	0.3142(2)	0.1661(2)	0.4973(4)	2.98
C(14)	0.1505(2)	0.0667(1)	0.2908(4)	2.56
C(15)	0.1681(3)	0.0364(2)	0.2080(4)	3.70
C(16)	0.1490(4)	−0.0117(2)	0.2024(5)	4.50
C(17)	0.1139(4)	−0.0295(2)	0.2785(5)	4.72
C(18)	0.0953(4)	−0.0005(2)	0.3584(5)	4.43
C(19)	0.1131(3)	0.0479(2)	0.3640(4)	3.32
C(20)	0.1047(2)	0.2483(1)	0.1560(4)	2.78
C(21)	0.1873(2)	0.2623(2)	0.2390(4)	3.16
C(22)	0.0588(2)	0.2630(2)	0.0341(4)	3.43
C(23)	0.0140(2)	0.2406(1)	0.4995(4)	2.21
C(24)	0.0852(3)	0.2430(2)	0.6216(4)	3.25
C(25)	0.1416(2)	0.1493(1)	0.5168(4)	2.60
C(26)	0.1413(14)	0.4536(8)	0.2405(2)	11.25
C(27)	0.1534(11)	0.4311(7)	0.1434(2)	9.05
C(28)	0.0857(10)	0.4021(6)	−0.0488(17)	7.99
C(29)	0.0000	0.3680(8)	0.7500	7.58

[a] O(3) and C(26)–C(29) refer to the solvate molecules.

and at CO and H_2 pressures of 28 atm, **7** and **8** were transformed into the corresponding aldehydes with greater than 95% yield within 0.5–2 h in the presence of **1**, **2**, **4** or **5**, and within 5–6 h when **3** or **4** was used as catalyst. At lower temperatures, however, the catalytic activity of the complexes proved to depend strongly on the structural features. The results of some representative experiments carried out with **7** and **8** at 70 and 90°C respectively are summarized in Table 6. This table indicates that the dinuclear catalysts **1** and **2**, containing 3-(diphenylphosphino)benzoic acid as tertiary phosphine ligands, are substantially more active than the monorhodium complexes **3** and **4**. This observation is in accordance with the Poilblanc's [14] proposal that dinuclear catalysts are superior to mononuclear catalysts. The electron-donating methyl groups proved to have only a small enhancing effect, as expected in terms of the well-known hydroformylation mechanism (see for example ref. 15).

TABLE 5. Selected bond length and angles for **6** with estimated standard deviations in parentheses

	Bond length (Å)		Bond length (Å)
Rh(1)–N(1)	2.102(3)	Rh(1)–N(2)	2.085(4)
Rh(1)–P(1)	2.256(1)	Rh(1)–C(25)	1.809(4)
P(1)–C(1)	1.840(4)	C(8)–C(13)	1.386(6)
P(1)–C(8)	1.826(4)	C(9)–C(10)	1.393(7)
P(1)–C(14)	1.829(4)	C(10–C(11)	1.378(8)
N(1)–C(20)	1.339(5)	C(11)–C(12)	1.371(7)
N(2)–C(23)	1.343(5)	C(12)–C(13)	1.391(6)
O(1)–C(7)	1.216(5)	C(14)–C(15)	1.404(6)
O(2)–C(25)	1.163(5)	C(14)–C(19)	1.381(6)
C(1)–C(2)	1.373(6)	C(15)–C(16)	1.391(7)
C(1)–C(6)	1.404(6)	C(16)–C(17)	1.368(9)
C(2)–C(3)	1.404(7)	C(17)–C(18)	1.368(9)
C(3)–C(4)	1.372(7)	C(18)–C(19)	1.395(7)
C(4)–C(5)	1.376(7)	C(20–C(21)	1.490(6)
C(5)–C(6)	1.396(6)	C(20–C(22)	1.378(6)
C(6)–C(7)	1.482(6)	C(23)–C(24)	1.488(6)
C(8)–C(9)	1.401(6)		
	Bond angle (°)		**Bond angle (°)**
N(2)–Rh(1)–N(1)	85.8(1)	P(1)–Rh(1)–C(25)	86.52(1)
P(1)–Rh(1)–N(1)	94.3(1)	N(2)–Rh(1)–C(25)	94.5(1)
C(8)–P(1)–C(1)	102.3(2)	C(10)–C(9)–C(8)	119.9(5)
C(14)–P(1)–C(1)	103.7(2)	C(11)–C(10)–C(9)	120.7(5)
C(14)–P(1)–C(8)	102.9(2)	C(12)–C(11)–C(10)	119.9(4)
C(2)–C(1)–P(1)	119.9(3)	C(13)–C(12)–C(11)	120.0(4)
C(6)–C(1)–P(1)	121.6(3)	C(12)–C(13)–C(8)	121.2(4)
C(6)–C(1)–C(2)	118.5(4)	P(1)–C(14)–C(15)	121.2(4)
C(3)–C(2)–C(1)	120.9(4)	P(1)–C(14)–C(19)	120.0(3)
C(4)–C(3)–C(2)	120.0(5)	C(15)–C(14)–C(19)	118.7(4)
C(5)–C(4)–C(3)	120.1(4)	C(14)–C(15)–C(16)	119.9(5)
C(6)–C(5)–C(4)	120.2(4)	C(15)–C(16)–C(17)	120.1(5)
C(5)–C(6)–C(1)	120.3(4)	C(16)–C(17)–C(18)	120.8(5)
C(7)–C(6)–C(1)	121.8(4)	C(17)–C(18)–C(19)	119.9(6)
C(7)–C(6)–C(5)	117.9(4)	C(14)–C(19)–C(18)	120.6(5)
O(1)–C(7)–C(6)	122.1(4)	N(1)–C(20)–C(21)	122.4(4)
C(9)–C(8)–P(1)	121.9(3)	N(1)–C(20)–C(22)	108.9(4)
C(13)–C(8)–P(1)	119.7(3)	C(21)–C(20)–C(22)	128.7(4)
C(13)–C(8)–C(9)	118.4(4)	N(2)–C(23)–C(24)	122.4(4)

TABLE 6. Hydroformylation of 1-dodecene (**7**) and cyclohexene (**8**) by catalysts **1–6** under comparable conditions [a]

Substrate	Catalyst	Conversion after 1 h (%)	Products [b] (yield (%))
7	1	51	**A** (32) **B** (18)
7	2	58	**A** (35) **B** (20)
7	3	2.1	**A** (1.3) **B** (0.8)
7	4	10	**A** (5) **B** (4)
7	5	8	**A** (5) **B** (3)
7	6	5	**A** (3) **B** (1.8)
8	1	37	**C** (37)
8	2	40	**C** (40)
8	3	11	**C** (9)
8	4	31	**C** (31)

[a] Reaction conditions as described in Section 3. The 1-dodecene was reacted at 70°C and the cyclohexene at 90°C. [b] **A**, $CH_3(CH_2)_{11}CHO$; **B**, $CH_3(CH_2)_9CH(CHO)CH_3$; **C**, $C_6H_{11}CHO$.

The low catalytic activities of **5** and **6** may be explained in terms of intramolecular oxidative addition, which results in the occupation of empty coordination sites. Since this process is reversed by an increase in the temperature, the activities of the formyl and carboxyl-containing catalysts become similar at 120°C.

Finally, it is note worthy that, under the conditions indicated in Table 6, hardly any side products are formed whereas, at 120°C, up to 30% of 1-dodecene is isomerized to 2-dodecene, which in turn forms the corresponding internal aldehydes. All six complexes catalyse the transformation of **7** to 1-undecanecarboxaldehyde in preference to the iso compound, although this regioselectivity is rather poor.

3. Experimental details

3.1. *Preparation of complexes 1–6*

As described by Usón *et al.* [8] for other rhodium pyrazolato complexes, a solution of two equivalents of the appropriate pyrazolate in 90% aqueous MeOH was treated with one equivalent of $[(COD)Rh(\mu\text{-}Cl)]_2$. The CH_2Cl_2 solution of the resulting precipitate was treated for 15 min with a stream of CO, followed by the addition of two equivalents of 2-(diphenylphosphino)benzoic acid [16], 3-(diphenylphosphino)benzoic acid [17] or (2-formylphenyl)diphenylphosphine [16]. When the evolution of CO had ceased, the solvent was evaporated and the residual complexes washed thoroughly with hexane.

The physical and analytical data for **2**, **4** and **6** were as reported previously [7].

Compound 1: melting point (m.p.), 294–300°C (decomposition). IR (Nujol): ν(RhC≡O) 1970, ν(C=O) 1710 cm^{-1}. Anal. Found: C, 54.75; H, 3.81; N. 5.38. $C_{46}H_{36}N_4O_6P_2Rh_2$ (1008.581) calc.: C, 54.78; H, 3.60; N, 5.56%.

Compound 3: m.p., 218–223°C (decomposition). IR (Nujol): ν 1950 cm^{-1}. Anal. Found: C, 54.44; H, 3.62; N, 5.40. $C_{23}H_{18}N_2O_3PRh$ (504.292) calc.: C, 54.78, H, 3.60; N, 5.56%.

Compound 5: m.p., 272–278°C (decomposition). IR (Nujol): ν(RhC≡O) 1935, ν(C=O) 1685 cm^{-1}. Anal. Found: C, 56.35; H, 3.68; N, 5.53. $C_{46}H_{36}N_4O_4P_2Rh_2$ (976.583) calc.: C, 56.58; H, 3.72; N, 5.74%.

3.2. X-ray crystal analyses of 3 and 6

Data collection was carried out with an Enraf–Nonius CAD-4 automatic diffractometer controlled by a μ-VAX II computer and fitted with low temperature equipment. The cell parameters were obtained from the angles of 25 reflections in the range $16° < 2\theta < 22°$ for **3** and $19° < 2\theta < 22°$ for **6**. Reflections were scanned with variable scan time, depending on the intensities, with two thirds of the time used for scanning the peak, a sixth for measuring the left-hand background and a sixth for measuring the right-hand background. The intensities of three reflections were checked every 2 h; the total loss of intensity during the entire period of data collection was 2.0% for **3** and 2.3% for **6**. The crystal orientation was checked every 200 intensity measurements by scanning three reflections. A new orientation matrix was automatically calculated from a list of 25 recentred reflections when the angular change was greater than 0.1%. The crude data were corrected for Lorentz and polarization effects [18]. The positions of the rhodium atoms were determined from a three-dimensional Patterson synthesis in space group $C2/c$ for both compounds. The calculated difference Fourier maps revealed all the missing carbon, nitrogen, phosphorus and oxygen atoms. The hydrogen positions were included in calculated positions with isotropic temperature factors. Several least-squares cycles minimized the quantity $\Sigma w(|F_o| - |F_c|)$. Atomic scattering factors and anomalous dispersion terms for C, N, P and O and scattering factors for H were taken from the literature [19–21]. Data reduction was performed using the SDP software package [22]. All other calculations were taken from SHELX 76 [23].

The discrepancy indices and other pertinent crystallographic data are shown in Table 1. Selected positional parameters, bond lengths and angles are given in Tables 2–5. Lists of positional parameters for the hydrogen atoms, of anisotropic thermal parameters and of structure factors for **3** and **6** have been deposited at the Fachinformationszentrum, Karlsruhe under depository number CSD-58105.

3.3. General procedure for hydroformylation of alkenes

A mixture of 2 mmol of the alkene, 6.7×10^{-3} mmol of the catalyst and 1 ml of toluene was placed in a glass-lined mini-autoclave fitted with a magnetic stirrer. The sealed autoclave was purged with argon and charged with CO at 28 atm and H_2 at 28 atm and then placed in an oil bath thermostatted at the desired temperature. After 1–2 h the mixture was cooled and analysed by both ^1H nuclear magnetic resonance spectroscopy and gas chromatography. Typical results are summarized in Table 6.

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