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Synthesis and X-ray powder diffraction characterization of $(OC)_2RhCl_2Rh(cod)$ (cod = cycloocta-1,4-diene)

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In order to elucidate the nature and the structure of the elusive $(OC)_2Rh(Ph_3SiO)_2Rh(cod)$ (cod) = cycloocta-1,5-diene) complex, an important model compound for surface catalysis, $(OC)_2RhCl_2Rh(cod)$ has been synthesized, and structurally characterized by *ab initio* X-ray powder diffraction. Crystals of $(OC)_2RhCl_2Rh(cod)$ are monoclinic, space group $P2_1/c$, $a = 6.659(1)$, $b = 12.274(1)$ and $c = 16.096(1)$ Å, $\beta = 92.176(5)°$, $Z = 4$, $\rho_{calc} = 2.209$ g cm^{-3}. The structure has been solved, from powder diffraction data only, by Patterson and Fourier-difference methods and has been ultimately refined, by the Rietveld method, down to $R_p = 0.116$ and $R_{wp} = 0.154$ for 4050 data points collected in the 12–93° (2θ) range. The molecule contains two square-planar rhodium atoms, one bearing two terminal carbonyls and the other bound to the chelating cod fragment, and two chlorine atoms bridging the Rh $\cdots$ Rh vector. The Rh_2Cl_2 core is markedly non-planar, the dihedral angle about the Cl $\cdots$ Cl hinge being 135.4(6)°.

The 'two-dimensional chemistry'[1] observed with transition-metal complexes supported on oxides is one of the most active sectors of research dealing with transition-metal catalysts.[2] In particular many aspects of the surface chemistry of rhodium, one of the most effective catalysts,[3] were studied, including the synthesis of model complexes of supposed surface species[4] and the interconversion of Rh complexes on oxide surfaces.[4c,5] Recently these latter studies have proved to be the basis of an efficient cluster synthesis.[6]

In the course of our earlier efforts in preparing models of surface species of rhodium, we observed[7] that the complexes $(OC)_2Rh(Ph_3SiO)_2Rh(CO)_2$ and $(cod)Rh(Ph_3SiO)_2Rh(cod)$ (cod = cycloocta-1,5-diene) are easily interconvertible. Now we report on the formation of an intermediate of this reaction, $(OC)_2Rh(Ph_3SiO)_2Rh(cod)$, which is fairly unstable in solution and cannot be satisfactorily characterized by spectroscopic methods. We were unable to grow suitable single crystals (for X-ray diffraction) of such an important intermediate; therefore, as indirect evidence of its nature, we decided to synthesize and structurally characterize its dichloro-bridged analogue, *i.e.* $(OC)_2RhCl_2Rh(cod)$. Unfortunately, this latter compound did not afford crystals of suitable quality but, given its lower complexity, it was decided to attempt its complete structural analysis on the basis of *ab initio* powder diffraction analysis, which has been recently shown to be a powerful technique for assessing the crystal and molecular structures of molecular and/or polymeric co-ordination compounds.[8,9]

Experimental

All operations[10] were carried out under a carefully dried, deoxygenated and CO_2-free Ar or CO atmosphere, using dried, deoxygenated solvents. Infrared spectra were recorded on IR-75 (Carl Zeiss, Jena, Germany) and Bruker FT-IR IFS 113V instruments. Proton and ^{13}C NMR spectra were obtained with Bruker AMX and AC200 spectrometers.

Starting materials were of commercial origin, except for $(Ph_3SiO)_2Rh(CO)_4$,[7] $(Ph_3SiO)_2Rh_2(cod)_2$,[7] $Cl_2Rh_2(CO)_4$,[11] $Cl_2Rh_2(cod)_2$[12] (from commercial $RhCl_3 \cdot xH_2O$) and Ph_3SiONa,[13] which were prepared according to published procedures.

Preparation of $Cl_2Rh_2(CO)_2(cod)$ 5 by reaction (*i*)

The complex $Cl_2Rh_2(cod)_2$ (100 mg, 0.20 mmol) was dissolved in dry *n*-hexane (50 cm^3) while being stirred under an Ar atmosphere at 50 °C in a Schlenk vessel, which was then left to cool to room temperature (r.t.). To this stirring solution was added at once a solution of $Cl_2Rh_2(CO)_4$ (78 mg, 0.20 mmol) in *n*-hexane (10 cm^3). The color of the initial yellow solution immediately turns orange and the IR ν(CO) spectrum of a sample shows almost exclusively the emergence of a new, two-component band system and some remaining (<10%) signals of $Cl_2Rh_2(CO)_4$.[14] The solution was then cooled to −80 °C for 4 h. Orange-yellow microcrystals were obtained. They were subsequently recrystallized from *n*-pentane (two to three times) to yield pure crystalline $Cl_2Rh_2(CO)_2(cod)$. Yield 160–170 mg (90–96%) for the crude and 140-150 mg (79–84%) for the recrystallized product (Found: C, 28.1; H, 2.9; Cl, 15.7; Rh, 46.5. Calc. for $C_{10}H_{12}Cl_2O_2Rh_2$: C, 27.24; H, 2.74; Cl, 16.08; Rh, 46.68%). IR [ν(CO), *n*-hexane] 2089vs, 2022vs cm^{-1}. ^1H NMR (C_6D_6, *vs.* $SiMe_4$): δ 4.2 (s, br, 4 H, CH), 2.0 (m, 4 H, CH*H*), 1.3 (m, 4 H, C*H*H). ^{13}C-{^1H} NMR (C_6D_6, *vs.* $SiMe_4$): δ 179.0 (CO, $J_{C–Rh}$ 73), 79.2 (CH, $J_{C–Rh}$ 11 Hz), 30.2 (CH_2).

Preparation of $(Ph_3SiO)_2Rh_2(CO)_2(cod)$ 6 by reaction (*i*)

The complex $(Ph_3SiO)_2Rh_2(CO)_2(cod)$ **6** was prepared similarly to **5** from 0.2 mmol quantities of $(Ph_3SiO)_2Rh_2(cod)_2$ and $(Ph_3SiO)_2Rh_2(CO)_4$. Yields >90% for the crude and 75–80% for the recrystallized product (Found: C, 60.3; H, 4.8; Rh 22.3.

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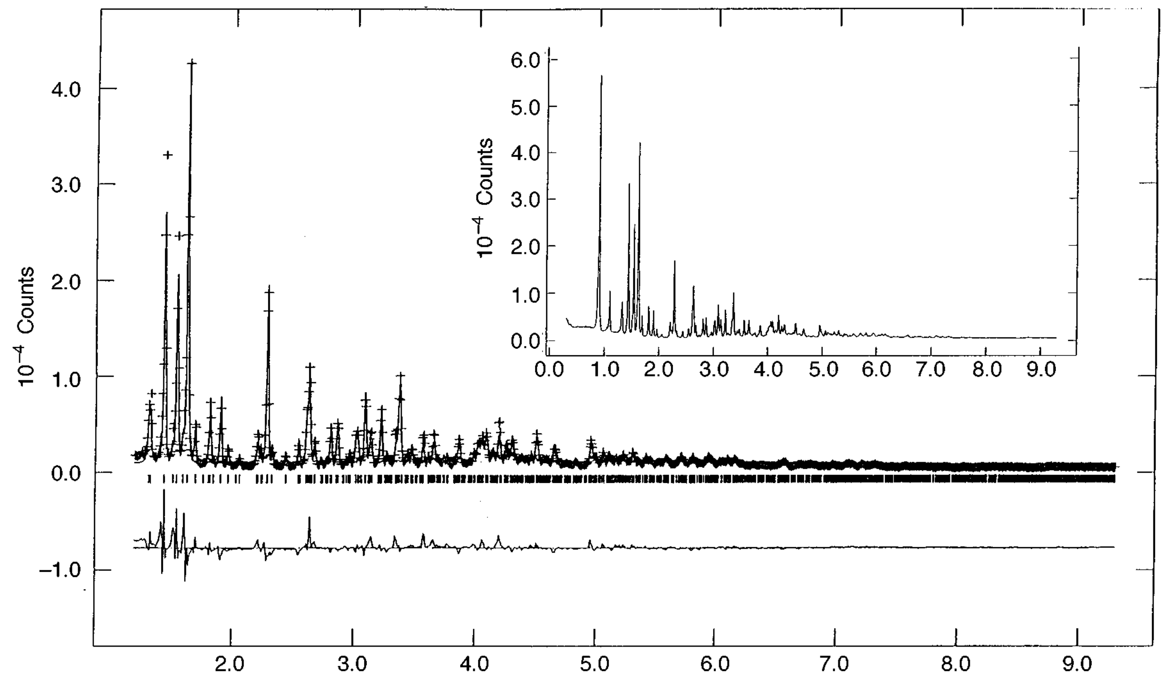


Fig. 1 Rietveld refinement plot for polycrystalline $(OC)_2RhCl_2Rh(cod)$ in the $12 < 2\theta < 93°$ range. Reflection markers and difference plot are also included. The insert shows the full raw data

Calc. for $C_{46}H_{42}O_4Rh_2Si_2$: C, 60.00; H, 4.60; Rh, 22.35%). IR [ν(CO), *n*-hexane] 2078vs, 2015vs cm^{-1}. ^1H NMR (C_6D_6, *vs.* $SiMe_4$): δ 7.97, 7.66, 7.24 (m, 30, CH, Ph), 4.18 (br s, 4 H, CH), 1.97 (br m, 4 H, CH*H*), 1.24 (br m, 4 H, C*H*H). ^{13}C-{^1H} NMR (C_6D_6, *vs.* $SiMe_4$): δ 180.1 (CO, $J_{C\text{-}Rh}$ 76), 138.0, 136.8, 136.1, 130.8 (CH, Ph), 79.8 (CH, $J_{C\text{-}Rh}$ 13 Hz), 31.3 (CH_2).

Preparation of $(Ph_3SiO)_2Rh_2(CO)_2(cod)$ 6 by reaction (*ii*)

The complex $(Ph_3SiO)_2Rh_2(CO)_4$ **4** (4 mg, 0.05 mmol) was dissolved in dry *n*-hexane (10 cm^3). To this solution, while stirring at r.t. under an Ar atmosphere, cycloocta-1,5-diene C_8H_{12} (52.0 μl, 45.9 mg, 0.085 mmol, 1.7 equivalents with respect to Rh_2) was added in three to four portions during 10 min periods. The reaction mixture was then stirred for an additional 15–20 min. A sample taken for spectroscopic analysis [IR, ν(CO) region] showed almost complete disappearance of the absorption bands of **4**, while the ν(CO) bands of **6** were practically those of the sole metal carbonyl species observed. The (spectroscopic) yield was calculated to be higher than 90%. Complex **5** could be prepared analogously from **3** and 1.5–1.7 molar excess of cod, yield >95%.

Preparation of $Cl_2Rh_2(CO)_4$ 3 by reaction (*iii*)

The complex $Cl_2Rh_2(CO)_2(cod)$ **5** (44 mg, 0.1 mmol) was dissolved in dry *n*-hexane (10 cm^3) under an Ar atmosphere. Over this solution, while stirring at r.t., the atmosphere was changed to a 1 : 1 mixture of Ar + CO. An immediate color change to orange was observed. The infrared spectroscopic analysis of the reaction mixture showed complete conversion of **5** into **3** after 10 min. The same method for transforming **6** into **4** yielded 30–40% of complex **6**, accompanied by the formation of 20–30% of $Rh_6(CO)_{16}$.[15] We observed that if the gases were not perfectly dry, humidity caused the formation of even higher quantities of $Rh_6(CO)_{16}$. Using non-diluted CO also favoured the formation of the latter compound.

Preparation of $(Ph_3SiO)_2Rh_2(CO)_2(cod)$ 6 by ion metathesis [reaction (*iv*)]

The complex $Cl_2Rh_2(CO)_2(cod)$ **5** (44 mg, 0.1 mmol) was dissolved in dry *n*-hexane (10 cm^3) under an Ar atmosphere. To this solution, while stirred at r.t. Ph_3SiONa (66 mg, 0.22 mmol) was added in two to three portions during 15–20 min. The solution was analysed by infrared ν(CO) spectroscopy after 20, 40 and 60 min. After 40 min, the spectra showed the formation of *ca.* 80% of **6** which did not change after 60 min. Reaction (*iv*) was also followed by ^1H NMR spectroscopy, using C_6D_6 as solvent.

X-ray powder diffraction of $(OC)_2RhCl_2Rh(cod)$

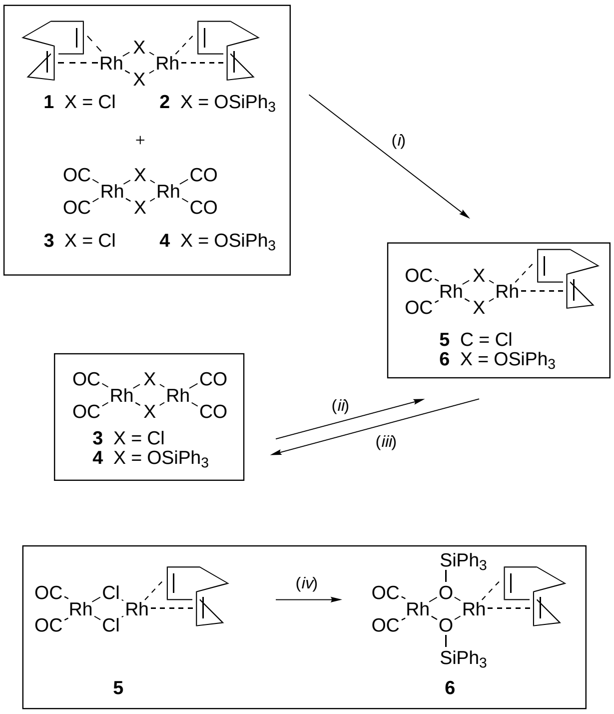
The orange powder was deposited, with the aid of silicon grease, on a silicon monocrystal cut normal to 511, minimizing the scattering from the substrate. Given the limited amount of the available material, the 'infinitely thick' limit, which allows absorption corrections in Bragg–Brentano geometry to be neglected, could not be reached; therefore, the average isotropic 'thermal' parameter, which is known to absorb most θ-dependent systematic errors, may be slightly overestimated. The sample was rotated at about 60 rpm about the scattering vector in order to minimize preferred orientation effects. The spectrum was collected under a nitrogen atmosphere to prevent sample decomposition. X-Ray powder diffraction (XRPD) data were taken with Cu-Kα radiation ($\lambda = 1.5418$ Å) on a Rigaku D III/MAX horizontal scan powder diffractometer equipped with parallel Soller slits and a graphite monochromator in the diffracted beam. Data were collected in the $3 < 2\theta < 93°$ range, in the θ–2θ mode and step scan with $\Delta 2\theta = 0.02°$ and $t = 12$ s. Slits used: DS, 1.0°; AS, 1.0°; RS, 0.15°. Standard peak-search methods were used to locate the diffraction maxima.

Indexing was performed using DICVOL 91[16] [$a = 6.66$, $b = 12.27$, $c = 16.10$ Å; $\beta = 92.18°$; M(15) = 34.4; F(15) = 71.1 (0.007, 28)]. The space group $P2_1/c$ was chosen from systematic absences and subsequently confirmed by satisfactory refinement. The integrated intensities were extracted by Le Bail's method,[17] using EXTRA;[18] the Rh atoms were located from a Patterson synthesis, while the Cl, C, O and N atoms were located from Fourier-difference maps and model building techniques. The final refinements were performed using the Rietveld method of GSAS[19] and restraining Rh–C–O and Rh–cod fragments to known geometries. A single isotropic atomic displacement parameter was refined from the rhodium and chlorine atoms [$U_{iso} = 0.067(2)$ Å^2], while light(er) atoms were

Table 1 Crystal data and refinement details for (OC)$_2$RhCl$_2$Rh(cod)

Compound	(OC)$_2$RhCl$_2$Rh(cod)
Formula	$C_{10}H_{12}Cl_2O_2Rh_2$
M_r/g mol^{-1}	440.8
System	Monoclinic
Space group	$P2_1/c$
a/Å	6.659(1)*
b/Å	12.274(1)
c/Å	16.096(1)
β/°	92.176(5)
U/Å^3	1314.7(2)
Z	4
F(000)	840
ρ_{calc}/g cm^{-3}	2.209
Radiation (λ/Å)	Cu-Kα (1.5418)
2θ Range/°	12–93
Scan mode	θ:2θ
No. of parameters	4050
No. of reflections	1133
R_p	0.116
R_{wp}	0.154
R_F	0.085

* Estimated standard deviations of lattice parameters are derived from the whole-pattern Rietveld refinement.



Scheme 1

assigned the same value arbitrarily raised by 0.020 Å^2. A more detailed description of the *ab initio* XRPD methodology applied to moderately complex *molecular* crystals can be found in ref. 20. Crystal data and refinement details are reported in Table 1. A final plot of the Rietveld refinement is shown in Fig. 1.

CCDC reference number 186/722.

Results and Discussion

Synthesis

Scheme 1 pictorially shows the different routes and alternative methods employed in the preparation of complexes Cl$_2$Rh$_2$(CO)$_2$(cod) and (Ph$_3$SiO)$_2$Rh$_2$(CO)$_2$(cod), together with the numbering scheme adopted for all reactants and products.

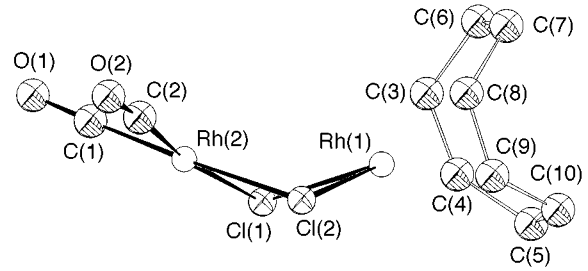


Fig. 2 An ORTEP[21] drawing of the (OC)$_2$RhCl$_2$Rh(cod) molecule, with partial labelling scheme. Relevant bond distances (Å) and angles (°): Rh(1)···Rh(2) 3.252(7), Rh(2)···Rh(2′) 3.55(1), Rh(1)–Cl(1) 2.409(4), Rh(1)–Cl(2) 2.400(4), Rh(2)–Cl(1) 2.396(13), Rh(2)–Cl(2) 2.409(13); Rh(1)–Cl(1)–Rh(2) 85.2(4), Rh(1)–Cl(2)–Rh(2) 85.1(3) [Rh(2′) is centrosymmetrically related to Rh(2)]

The high yield syntheses from *symmetrically substituted* bis(diolefinic) (**1** or **2**) and tetracarbonyl (**3** or **4**, respectively) derivatives clearly indicate that compounds **5** and **6** are the thermodynamically favoured products in the reaction mixture, to an extent which is significantly larger than that foreseen by purely entropic (configurational, *i.e.* 'mixing') arguments. This implies a small enthalpic stabilization of **5** (and **6**), possibly due to the larger polarity of the mixed-ligand derivatives. The observed 'instability' to moisture and/or air contamination (in solution *and* in the solid state), which increases with the carbonyl content in the order **1** < **5** < **3** (and, similarly, for siloxy derivatives, **2** < **6** < **4**), could be related to the availability of easy degradation paths leading to stable carbonyl clusters [*e.g.* Rh$_6$(CO)$_{16}$] but not to homoleptic poly(olefinic) derivatives.

Crystallography

As repeated attempts to grow single crystals of **5** suitable for conventional X-ray diffraction methods failed, affording either very small (maximum dimensions 20 × 20 × 100 μm), thus poorly diffracting and untreatable (single?) crystals or macroscopic aggregates of polycrystalline nature, we decided to characterize **5** *via* XRPD. Note that, in principle, we could also have attempted an XRPD characterization of **6**; however, the foreseen asymmetric unit volume of its crystalline phase (1015 Å^3, obtained by averaging that of **2** and **4**)[7] was discouraging, while that of **5** (328 Å^3, obtained by averaging that of **1** and **3**)[21] was not.

X-Ray powder diffraction methods revealed that **5** contains two square-planar Rh atoms (see Fig. 2), one bearing two terminal carbonyls and the other bound to the chelating cod fragment (chelating, four-electron donors, η^2,η^2-cod ligands, being idealized by two pseudo-atoms located at the midpoints of the C=C bonds), joined by two chlorine atoms bridging the Rh···Rh vector [Rh···Rh 3.252(7) Å; average Rh–Cl 2.40(1) Å]. The Rh$_2$Cl$_2$ core is markedly non-planar, the dihedral angle about the Cl···Cl hinge being 135.4(6)°, thus resembling much more of the geometry of (OC)$_2$RhCl$_2$Rh(CO)$_2$ [126.8(3)°],[22a] rather than that of the (cod)RhCl$_2$Rh(cod) (180°)[22b] analogues. Note that L$_2$M(μ-X)$_2$ML$_2$ fragments (M = Co, Rh or Ir; X = Cl, Br, I, OR, SR or PR$_2$; L = any two-electron donor ligand), based on square-planar metal centers, are known to belong to two distinct structural types, containing essentially planar or *markedly* bent M$_2$X$_2$ cores, respectively, while intermediate conformers are lacking; this bimodal distribution shows two *well separated* peaks: a very sharp one for 'planar' conformations and a broader one for bent fragments, mainly reflecting the variety of bridging (μ-X) and ancillary (L) ligands. As a consequence, since **5** does not belong to the 'planar' class (for reasons which are not yet understood), it is not surprising that it shows a dihedral angle similar to that of (OC)$_2$RhCl$_2$Rh(CO)$_2$.

If the presence of short Rh···Rh intermolecular contacts is taken as a criterion of similarity, **5**, which packs as 'dimers' [Rh(2)···Rh(2′) 3.55(1) Å], is intermediate between

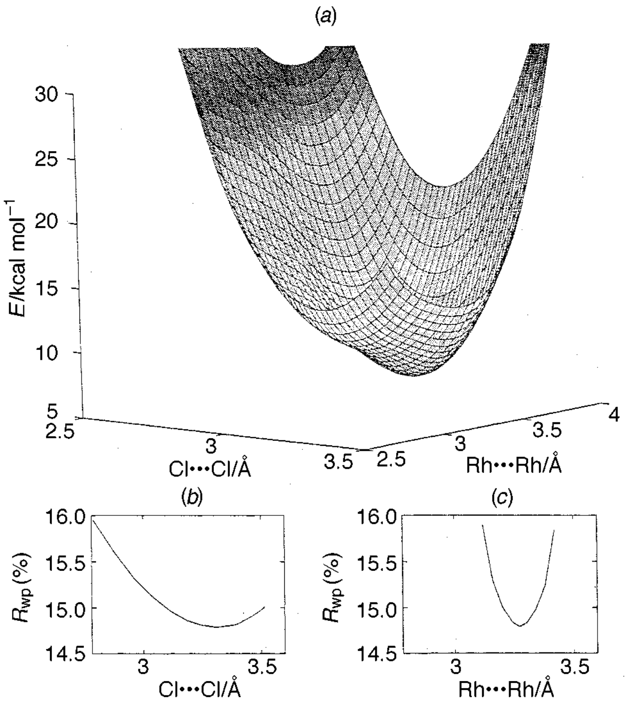


Fig. 3 (*a*) A three-dimensional view of the potential energy hypersurface (kcal mol^{-1}, cal = 4.184 J), projected onto the Rh···Rh *vs.* Cl···Cl plane (values in Å); (*b*) and (*c*): monodimensional cuts of the R_{wp} hypersurface along the Rh···Rh and Cl···Cl directions, respectively

$(OC)_2RhCl_2Rh(CO)_2$ and (cod)$RhCl_2Rh$(cod). Indeed, while the former is a 'polymer' with Rh···Rh contacts of 3.31 Å, no short interactions are observed in the latter. A closer analysis shows that short contacts invariably involve the Rh atoms bound to carbonyls, thus suggesting that the presence of (bulky) cod ligands requires long(er) Rh···Rh contacts.

As meaningful Rietveld XRPD refinements require introduction of numerous constraints on the geometrical values of chemically known fragments, at least when working with conventional instrumentation, only the packing and conformations of the molecules, together with the heavy atom locations, can be assessed with reasonable accuracy. The introduction of constraints normally drives the 'molecular' shape toward an idealized conformation with loss of structural details (which are anyway unaccessible by PD) but hardly control intermolecular contacts. For instance, at the end of the refinement we still observe a rather short packing contact [namely, O(1)···O(1′) 2.67(6) Å] which could be easily relaxed by small, but unpredictable, structural changes.

For this reason, we have further checked the obtained results by minimizing the steric energy of different molecular conformations *in the actual crystal lattice*, with a locally developed[23] version of Allinger's MM3 program.[24] On adopting the empirical force field for π-bonding ligands discussed in ref. 25, avoiding any bias toward the planar or bent conformations at the *intra*molecular level, all deformation paths of the central Rh_2Cl_2 butterfly from the geometry determined by XRPD substantially raised the overall (*intra*molecular + packing) steric energy; this is pictorially shown in Fig. 3(*a*), which contains a section of the potential energy hypersurface along the Cl···Cl and Rh···Rh coordinates, all other degrees of freedom being optimized at each (hyper)point. This does not imply that the observed stereochemistry is dictated by packing constraints but, rather, that the *experimentally accessible* lattice parameters and symmetry *alone* may contain useful information on the molecular stereochemistry. For instance, in the present case, at the resolution stage where only the Rh_2Cl_2 core was known, we could immediately devise which rhodium atom was bound to cod by simple packing considerations. Such information could be, in principle, exploited by *joint* Rietveld/steric energy/packing energy refinements, but this feature has not been implemented on currently available programs. The common use of restraints in complex Rietveld refinements (ensuring chemical significance to the derived parameters), normally obtained by introducing new observational equations of geometrical nature, may be interpreted as a *very rough* approach of optimization of a few *intra*molecular degrees of freedom. Within the GSAS approach, this corresponds to harmonic potential wells for stretching modes (bond distances) with *arbitrary* force constants; since bond angles and torsions cannot be restrained, 1,3 and 1,4 distances may be, in principle, included. However, if the minima of the two cost functions (R_{wp} in the Rietveld refinement and E_{tot} in the MM program) are close, as in the present case [compare Fig. 3(*a*) with the monodimensional cuts of R_{wp} surface reported in Fig. 3(*b*) and 3(*c*)], even independent Rietveld and steric energy/packing energy refinements can be used to confirm the reliability of the proposed molecular conformation. A similar approach, involving only *inter*molecular (*i.e.* packing and electrostatic) energies and very limited diffraction data sets (2θ < 30°, Cu-Kα radiation), has been used for structural analysis of the monoclinic polymorph of titanophthalocyanine.[26] Note that our computations represent only a shortcut to the correct approach (the joint refinement) since, even if the two minima match (which is not always true, mainly because of the intrinsic weakness of the force field), their curvatures may not. Indeed, R_{wp} is much more sensitive to the Rh···Rh than to the Cl···Cl deformation [compare Fig. 3(*b*) and 3(*c*)], since it is more 'expensive' to displace high *Z* atoms, contributing the most to the diffraction pattern. Conversely, from Fig. 3(*a*), it is clear that the potential energy hypersurface is softer along the Rh···Rh direction rather than along the Cl···Cl.

Conclusion

The preparation of complexes **5** and **6** complements our earlier observations about the formation of dinuclear rhodium carbonyl complexes with *two different* anions in the bridging position.[4b]

The existence of complexes **5**, and especially **6**, is of an additional significance, since it shows that the greatest care should be taken on formulating the Rh-containing surface species; indeed, as demonstrated earlier[7] and in this work, the actual ligand environment of rhodium is found to be very sensitive to the reaction conditions.

Once again, XRPD (from conventional laboratory equipment) has been proven to be a useful tool in addressing structural problems which have no easy solution with standard techniques. As a matter of fact, it is likely that new instrumentation and sources (high brilliance synchrotrons and time of flight neutrons) will soon raise the complexity of the organometallic molecules which can be characterized by PD. Nevertheless, even in the future, it will be the daily use of easily accessible conventional instrumentation which will provide the organometallic chemistry community with *otherwise inaccessible* structural results,[8] well beyond the conventional use of XRPD as an 'analytical' tool.

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References

1 G. A. Somorjai, *Chemistry in Two Dimensions: Surfaces*, Cornell University Press, Ithaca, 1981; G. A. Somorjai, *Introduction to Surface Chemistry and Catalysis*, Wiley, New York, 1994.

2 R. Psaro and R. Ugo, *Metal Clusters in Catalysis*, eds. B. C. Gates, L. Guczi and H. Knötzinger, Elsevier, Amsterdam, 1986, p. 427; H. H. Lamb, B. C. Gates and H. Knötzinger, *Angew. Chem.*, *Int. Ed. Engl.*, 1988, **27**, 1127; J. M. Basset, B. C. Gates, J. P. Candy, A. Choplin, M. Lecomte, F. Quignard and C. Santini (Editors), *Surface Organometallic Chemistry: Molecular Approaches to Surface Catalysis*, Kluwer, Dordrecht, 1988; R. Psaro, D. Roberto, R. Ugo, C. Dossi and A. Fusi, *J. Mol. Catal.*, 1992, **74**, 391.

3 L. Marko, *Aldehyde (methoden der Organischen Chemie*, *Houben-Weyl)*, ed. J. Falbe, Thieme, Stuttgart, 1983, vol. E3, p. 224; F. H. Jardine, *The Chemistry of the Metal-Carbon Bond*, ed. F. R. Hartley, J. Wiley, New York, 1987, vol. 4, p. 733, 1049; D. Parker, *ibid.*, p. 979; F. R. Hartley, *ibid.*, p. 1163; V. Ponec, *New Trends in CO Activation*, ed. L. Guczi, Elsevier, Amsterdam, 1991, p. 117; C. H. Batholomew, *ibid.*, p. 158; H. M. Colquhoun, D. J. Thompson and M. W. Twigg, *Carbonylation*, Plenum Press, New York, 1991; R. J. Farruto, R. M. Heck and B. K. Speronello, *Chem. Eng. News*, 1992 (Sept. 7), 34.

4 (*a*) A. Vizi-Orosz, G. Pályi and L. Marko, *J. Organomet. Chem.*, 1973, **57**, 379; (*b*) G. Pályi, A. Vizi-Orosz, L. Marko, F. Marcati and G. Bor, *J. Organomet. Chem.*, 1974, **66**, 295; (*c*) A. Theolier, A. K. Smith, M. Lecomte, J. M. Basset, G. M. Zanderighi, R. Psaro and R. Ugo, *J. Organomet. Chem.*, 1980, **191**, 415; (*d*) A. Vizi-Orosz and L. Marko, *Transition Met. Chem.*, 1982, **7**, 216; (*e*) G. Pályi, C. Zucchi, R. Ugo, R. Psaro and A. Sironi, *J. Mol. Catal.*, 1992, **74**, 51.

5 A. K. Smith, F. Hughes, A. Theolier, J. M. Basset, R. Ugo, G. M. Zanderighi, J. L. Bilhou, W. Bilhou-Bougnol and W. F. Gray, *Inorg. Chem.*, 1979, **18**, 3104; J. L. Bilhou, W. Bilhou-Bouguol, W. F. Graydon, A. K. Smith, J. M. Basset, G. M. Zanderighi and R. Ugo, *J. Organomet. Chem.*, 1978, **153**, 73.

6 D. Roberto, E. Cariati, R. Psaro and R. Ugo, *Organometallics*, 1994, **13**, 734.

7 A. Vizi-Orosz, R. Ugo, R. Psaro, A. Sironi, M. Moret and G. Pályi, *Inorg. Chem.*, 1994, **33**, 4600.

8 For recent review papers, see: K. D. M. Harris and M. Tremayne, *Chem. Mater.*, 1996, **8**, 2554; N. Masciocchi and A. Sironi, preceding paper.

9 R. E. Dinnebier, F. Olbrich and P. W. Stephens, *Acta Crystallogr.*, *Sect. B*, 1996, **53**, 153; D. Louër, M. Louër and R. Ceolin, *Acta Crystallogr.*, *Sect. B*, 1994, **51**, 82; N. Masciocchi, M. Moret, P. Cairati, F. Ragaini and A. Sironi, *J. Chem. Soc.*, *Dalton Trans.*, 1993, 471; N. Masciocchi, P. Cairati, F. Ragaini and A. Sironi, *Organometallics*, 1993, **12**, 4499; N. Masciocchi, M. Moret, P. Cairati, A. Sironi, G. A. Ardizzoia and G. La Monic, *J. Am. Chem. Soc.*, 1994, **116**, 7768; N. Masciocchi, M. Moret, P. Cairati, A. Sironi, G. A. Ardizzoia and G. La Monica, *J. Chem. Soc.*, *Dalton Trans.*, 1995, 1671; N. Masciocchi, M. Moret, A. Sironi, G. A. Ardizzoia, S. Cenini and G. La Monica, *J. Chem. Soc.*, *Chem. Commun.*, 1995, 1955; N. Masciocchi, G. A. Ardizzoia, G. La Monica, M. Moret and A. Sironi, *Inorg. Chem.*, 1997, **36**, 449.

10 D. F. Shriver and M. A. Drezdon, *The Manipulation of Air-Sensitive Compounds*, Wiley, New York, 2nd edn., 1986.

11 J. A. McCleverty and G. Wilkinson, *Inorg. Synth.*, 1966, **8**, 211.

12 G. Giordano and R. H. Crabtree, *Inorg. Synth.*, 1979, **19**, 218.

13 L. H. Sommer, E. W. Petrusza and F. C. Whitemore, *J. Am. Chem. Soc.*, 1946, **68**, 2283.

14 B. F. G. Johnson, J. Lewis and P. W. Robinson, *J. Chem. Soc. A*, 1969, 2693.

15 E. R. Corey, L. F. Dahl and W. Beck, *J. Am. Chem. Soc.*, 1963, **85**, 1202; L. Malatesta, G. Caglio and M. Angoletta, *Chem. Commun.*, 1970, 532.

16 A. Boultif and D. Louër, *J. Appl. Crystallogr.*, 1991, **24**, 987.

17 A. Le Bail, H. Duroy and J. L. Fourquet, *Mater. Res. Bull.*, 1988, **23**, 447.

18 A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, M. C. Burla and G. Polidori, *J. Appl. Crystallogr.*, 1995, **28**, 738.

19 A. C. Larson and R. B. Von Dreele, LANSCE, Ms-H805, Los Alamos National Laboratory, NM, 1990.

20 N. Masciocchi, P. Cairati and A. Sironi, *Powder Diffr.*, 1997, in the press.

21 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

22 (*a*) $Cl_2Rh_2(CO)_4$: L. F. Dahl, C. Martell and D. L. Wampler, *J. Am. Chem. Soc.*, 1961, **83**, 1761; L. Walz and P. Scheer, *Acta Crystallogr.*, *Sect. C*, 1991, **47**, 640; (*b*) $Cl_2Rh_2(cod)_2$: J. A. Ibers and R. G. Snyder, *Acta Crystallogr.*, 1962, **15**, 923; J. C. A. Boeyens, L. Denner, S. W. Orchard, I. Rencken and B. G. Rose, *S. Afr. J. Chem.*, 1986, **32**, 229.

23 P. Mercandelli, M. Moret and A. Sironi, unpublished work.

24 N. L. Allinger, Y. H. Yuh and J. H. Lii, *J. Am. Chem. Soc.*, 1989, **111**, 8551.

25 P. Mercandelli and A. Sironi, *J. Am. Chem. Soc.*, 1996, **118**, 11 548.

26 K. Oka, O. Okada and K. Nukada, *Jpn. J. Appl. Phys.*, *Part 1*, 1992, **31**, 2181.

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