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Isolation and structural characterization of an optically active intermediate in the oxidative addition of methyl iodide on a rhodium(I) centre†

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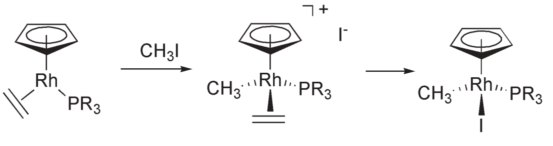
The optically pure cationic complex ((S,S_{Rh}))-[Rh(η^5-$C_5H_4CH_2CH(Ph)PPh_2$-κP)(η^2-CH_2CH_2)(CH_3)][I] is the first example of a key intermediate in the oxidative addition reaction of methyl iodide on a rhodium(I) centre which has been structurally characterized by X-ray diffraction.

Oxidative addition is a fundamental organometallic reaction step, which plays a key role in many catalytic processes.[1] In particular, the addition of CH_3I to carbonyl rhodium and iridium complexes has been studied in mechanistic detail, since it is the key step in the catalyzed carbonylation of methanol on an industrial scale.[2] On the basis of many studies, several mechanisms have been proposed for the oxidative addition reaction of alkyl halides. The most common mechanisms noted in the literature are the S_N2 and the concerted *cis*-addition mechanisms, and mechanisms involving free alkyl radical intermediates.[3] Recent theoretical and experimental studies of the oxidative addition of CH_3I to Pd, Rh, and Ir complexes suggest that the preferred pathway is S_N2 which occurs *via* a two-step mechanism involving (i) nucleophilic attack by the metal on the alkyl carbon to displace iodide and form a metal–carbon bond and (ii) coordination of iodide to the cationic alkyl intermediate.[4] Study of structure, isomerization, and reactivity of cationic methyl intermediates might shed more light on the mechanism of oxidative addition, but the high reactivity of these intermediates prevents their study directly in the reaction mixtures. A cationic methyl ethylene rhodium(III) species was first proposed by Oliver and Graham as the key intermediate originating from oxidative addition reaction of CH_3I on a cyclopentadienyl(triphenylphosphine)ethylene rhodium complex (Scheme 1).[5] The rapid conversion of this species to the methyl iodide rhodium(III) complex prevented its characterization. Werner and Feser were able to isolate the methyl ethylene intermediate in a similar system, but only after exchange of the iodide anion for the PF_6 anion.[6]

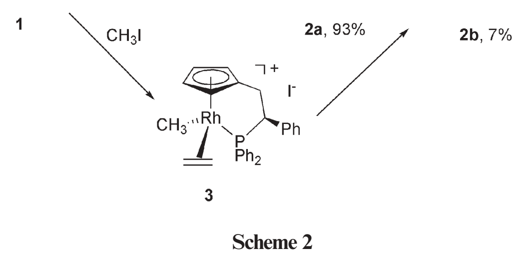
Cyclopentadienyl complexes bearing pendant ligands such as phosphine moieties are gaining increased attention.[7] We have investigated the chemistry of rhodium, ruthenium and iridium with chiral cyclopentadienyl-linked phosphine ligands.[8] In particular, we have already reported on the reactivity of rhodium ethylene and carbonyl complexes of chiral cyclopentadienyl–phosphine ligands in the oxidative addition reaction of CH_3I.[9]

We have found that complex **1** undergoes an oxidative addition reaction with CH_3I in THF at room temperature affording the two diastereomers **2a** and **2b** in a 93 : 7 ratio (86% de) (Scheme 2). The configuration around rhodium in the major diastereomer was found to be *S* by X-ray structural determination. A dramatic decrease in diastereoselectivity was observed when the reaction was performed in CH_2Cl_2: **2a** and **2b** were obtained with an 80 : 20 ratio (60% de). When the reaction was followed by ^{31}P NMR (THF or CH_2Cl_2 solution), some interesting features emerged. The signal of the parent complex **1** disappeared gradually ($^1J_{PRh}$ = 216 Hz), and the signal of a new species **3** appeared that showed a smaller coupling of 135 Hz with rhodium. After one hour at room temperature, the signal of **1** vanished and the only detectable signal was that one with the small coupling (either in THF or CH_2Cl_2). The reaction then went along affording eventually the expected products of the oxidative addition, **2a** and **2b**, in different diastereomeric ratios, which showed a coupling to rhodium of $^1J_{PRh}$ = 168 and 170 Hz respectively.



Scheme 1

It was possible to isolate the intermediate species **3**, in crystalline form suitable for X-ray structural determination, by performing the reaction in nitromethane. Fig. 1 shows the ORTEP view of **3** and important bond lengths and angles are summarized.‡ The configuration around the metal in **3** is the same as that one found in the major diastereomer of the oxidative addition, **2a**; that is, the methyl group is on the opposite side of the phenyl substituent of the chiral carbon of the linking chain. The formation of only one diastereomer of **3** can be rationalized looking at Fig. 2, where the space-filling diagrams of the crystal structure of **1** are displayed (see ESI for the diagrams of **2a** and **3**†). From the figure, the chiral pocket created by the phenyl groups of the phosphine can also be appreciated; one phenyl is almost parallel to the phenyl substituent on the bridge and shelters one side of the molecule. The first step in the oxidative addition is the nucleophilic attack on CH_3I by the electron rich metal, and it occurs from the less hindered side of the molecule. Then the intermediate cationic species reacts further, and, taking into account that it is an 18-electron saturated species, the most feasible way is to loose the ethylene ligand. The solvent can then occupy the vacant coordination site thus created; at this stage there is the possibility of partial epimerization that can explain why the final product is not diastereomerically pure and the difference observed in performing the reaction in solvents with very different ligating ability. Further studies are underway to clarify the transformation of **3** to **2a** and **2b**. A precise mechanistic discussion is premature. We believe that several mechanisms are involved, as



Scheme 2

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† Electronic supplementary information (ESI) available: typical experimental procedures, physical and spectroscopic data of all new compounds and space-filling diagrams of **1**, **2a** and **3**. See http://www.rsc.org/suppdata/cc/b4/b409134e/

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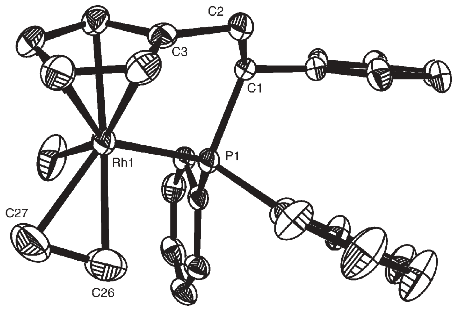


Fig. 1 An ORTEP drawing of **3** with 50% thermal ellipsoids. The iodide anion, the solvent molecule and hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°): Rh1–P1 2.2923(12), Rh1–C26 2.236(6), Rh1–C27 2.256(6), Rh1–C28 2.074(6), Rh1–C3 2.210(4), C1–P1–Rh1 102.81(13), P1–Rh1–C3 81.81(12), C2–C3–Rh1 117.9(3), P1–Rh1–C28 88.51(17), C27–Rh1–C26 35.4(2).

we observed the formation of small amounts of the diiodide [Rh(η^5-$C_5H_4CH_2CH(Ph)PPh_2$–κP)I_2], **4**. Since the methyl iodide was free of iodine initially, and **2a** and **2b** do not react further with CH_3I to give **4**, there should be a reaction that transforms **3** to **4**. Presuming that the partial epimerization of **3** could be due to loss of the ethylene group and creation of a vacant position at the metal, we synthesized a new ligand bearing a fluorenyl moiety, envisioning that the known ability of such groups to switch from an η^5- to an η^1-coordination,[10] would prevent the loss of ethylene, allowing coordination of the iodide ion, eventually yielding to complete diastereoselective control of the reaction. Indeed, we synthesized the fluorenyl complex **5**, and were delighted to observe the formation of only one diastereomer, **6**, in which the same configuration at the metal found in **2a** was observed, as determined by a NOE difference experiment, (Scheme 3). Also in this case, it was possible to observe only one diastereomer of an intermediate analogous to **3**, which evolved to the optically pure complex **6** as well as to small amounts of the diiodide complex.

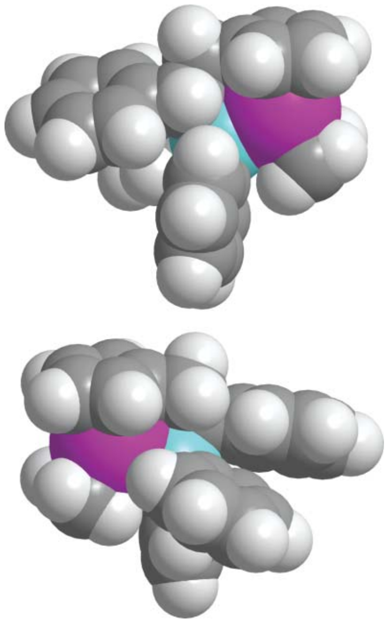
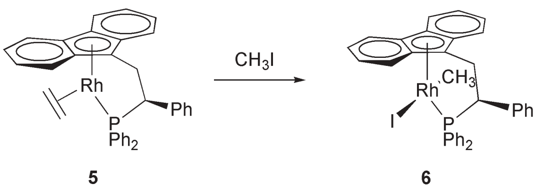


Fig. 2 Space-filling diagrams of **1**. Rhodium = purple, phosphorus = light blue.



Scheme 3

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Notes and references

‡ Crystal data: $3 \cdot CH_3NO_2$: $C_{29}H_{32}INO_2PRh$, $M = 687.34$, orthorhombic, space group $P2_12_12_1$, $a = 9.913(3)$, $b = 14.436(4)$, $c = 19.885(4)$ Å, $V = 2845.6(13)$ Å^3, $Z = 4$, $D_c = 1.604$ g cm^{-3}, μ(Mo–Kα) = 1.767 mm^{-1}, $F(000) = 1368$. Bruker SMART APEX CCD diffractometer with Mo–Kα radiation ($\lambda = 0.71073$ Å), 36867 intensities were collected with ω scans at 110(2) K on a dark red block-shaped crystal of 0.20 × 0.09 × 0.07 mm. 6499 independent reflections, structure solution by SHELXS97,[11] refinement by SHELXL97,[12] hydrogen atoms riding in standard positions, $R1$ [for 5900 reflections with $I > 2\sigma(I)$] 0.0360, $wR2$ (all data) 0.0799. Flack's enantiomorph polarity parameter[13] converged to −0.02(2). CCDC 242796. See http://www.rsc.org/suppdata/cc/b4/b409134e/ for crystallographic data in .cif or other electronic format.

1 (*a*) J. P. Collman, L. S. Hegedus, J. R. Norton and R. G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, CA, **5**, 1987; (*b*) Ch. Elschenbroich and A. Salzer, *Organometallics. A Concise Introduction*, VCH, Weinheim, Germany, 1992, ch. 17.
2 (*a*) D. Forster, *Adv. Organomet. Chem.*, 1979, **17**, 255; (*b*) M. J. Howard, M. D. Jones, M. S. Roberts and S. A. Taylor, *Catal. Today*, 1993, **18**, 325; (*c*) A. Haynes, B. E. Mann, G. E. Morris and P. M. Maitlis, *J. Am. Chem. Soc.*, 1993, **115**, 4093; (*d*) G. J. Sunley and D. J. Watson, *Catal. Today*, 2000, **58**, 293.
3 (*a*) S. Henderson and R. A. Henderson, *Adv. Phys. Org. Chem.*, 1987, **23**, 1; (*b*) J. A. Labinger and J. A. Osborn, *Inorg. Chem.*, 1980, **19**, 3230; (*c*) J. A. Venter, J. G. Leipoldt and R. van Eldik, *Inorg. Chem.*, 1991, **30**, 2207; (*d*) T. L. Hall, M. F. Lappert and P. W. Lednor, *J. Chem. Soc., Dalton Trans.*, 1980, 1448.
4 (*a*) T. R. Griffin, D. B. Cook, A. Haynes, J. M. Pearson, D. Monti and G. E. Morris, *J. Am. Chem. Soc.*, 1996, **118**, 3029; (*b*) F. M. Bickelhaupt, T. Ziegler and P. Von Ragué Schleyer, *Organometallics*, 1995, **14**, 2288.
5 A. J. Oliver and W. A. G. Graham, *Inorg. Chem.*, 1971, **6**, 1165.
6 H. Werner and R. Feser, *J. Organomet. Chem.*, 1982, **232**, 351.
7 (*a*) H. Butenschön, *Chem. Rev.*, 2000, **100**, 1527; (*b*) Y. Kataoka, Y. Iwato, T. Yamagata and K. Tani, *Organometallics*, 1999, **18**, 5423; (*c*) Y. Kataoka, Y. Nakagawa, A. Shibahara, T. Yamagata, K. Mashima and K. Tani, *Organometallics*, 2004, **23**, 2095.
8 (*a*) A. Doppiu, U. Englert and A. Salzer, *Inorg. Chim. Acta*, 2003, **350**, 435; (*b*) E. Becker, K. Mereiter, M. Puchberger, R. Schmid, K. Kirchner, A. Doppiu and A. Salzer, *Organometallics*, 2003, **22**, 3164; (*c*) A. Doppiu, U. Englert, V. Peters and A. Salzer, *Inorg. Chim. Acta*, 2004, **357**, 1773; (*d*) A. Doppiu and A. Salzer, *Eur. J. Inorg. Chem.*, 2004, 2244.
9 S. Ciruelos, A. Doppiu, U. Englert and A. Salzer, *J. Organomet. Chem.*, 2002, **663**, 183.
10 M. J. Calhorda and L. F. Veiros, *Comments Inorg. Chem.*, 2001, **22**, 375.
11 G. M. Sheldrick, *SHELXS97, Program for Crystal Structure Solution*, University of Göttingen, 1997.
12 G. M. Sheldrick, *SHELXL97, Program for Crystal Structure Refinement*, University of Göttingen, 1997.
13 H. D. Flack, *Acta Crystallogr. Sect. A*, 1983, **39**, 876.