Synthesis and Characterization of Novel Rhodium Porphyrin Derivatives with a Metal–Metal Bond

T. BOSCHI, S. LICOCCIA, R. PAOLESSE
and P. TAGLIATESTA

Dipartimento di Scienze e Tecnologie Chimiche, II Universita' di Roma 'Tor Vergata', 00173 Rome, Italy

(Received December 2, 1987)

In the last years much interest has been devoted to the synthesis and characterization of several metallo porphyrins which contain a metal–metal bond [1]. The main interesting aspects of such complexes are the mimesis of enzymes, as far as the biological field is concerned, and the potential use as new unidirectional conducting materials.

In recent papers [2–4] we have described the synthesis of novel rhodium porphyrinates with various axial ligands. Now we report the first examples of complexes of Rh(III)TPP containing a metal–metal bond with $Mn(CO)_5$, $Co(CO)_4$, $SnCl_3$ and $GeCl_3$ moieties. These bonded heterometallic complexes have been characterized by various spectroscopic techniques.

Experimental

IR spectra were recorded on a Perkin-Elmer Model 983 spectrophotometer as nujol mulls. NMR spectra were recorded on a Bruker WP 80 SY instrument as C_6D_6 or C_5D_5N solutions with tetramethylsilane (TMS) as internal standard. Electronic spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer as diethyl ether or tetrahydrofurane solutions.

RhTPPCl was prepared following the literature methods [5].

The syntheses were performed under a purified nitrogen atmosphere. The solvents (Farmitalia) were distilled under a nitrogen atmosphere from $LiAlH_4$ and immediately used.

Synthesis of TPPRhML

(a) ML = $Mn(CO)_5$, $Co(CO)_4$

A THF solution of metalate carbonyl anion (1.2 mmol) [6] is added to a THF solution of RhTPPCl (1 mmol) and the mixture is stirred for 12 h. The solvent is evaporated under reduced pressure and the residue is dissolved in diethyl ether. After filtration the solution is concentrated to about 10 ml and n-hexane is added (50 ml). Complexes precipitate as dark red crystals. Analytically pure products can be obtained by column chromatography on type I basic alumina (eluent Et_2O), but such a purification procedure leads to extensive decomposition for $TPPRhCo(CO)_4$.

(b) ML = $SnCl_3$

Anhydrous $SnCl_2$ (1.2 mmol) and RhTPPCl (1 mmol) are dissolved in THF and the solution is stirred overnight. The solvent is evaporated under reduced pressure and the residue worked up as above (a).

(c) ML = $GeCl_3$

NEt_4GeCl_3 (1.2 mmol) [7] and RhTPPCl (1 mmol) are dissolved in THF and solution is stirred overnight. The solvent is evaporated under reduced pressure and the residue worked up as above (a).

All elemental analysis gave satisfactory results in agreement with the theoretical values.

Results and Discussion

The synthesis of novel Rh(III) porphyrin derivatives was a natural extension of our work on the pyrrole macrocycles [2–4]; our aim was to explore the behaviour of the porphyrins as a ligand on the metal–metal bond. These type of complexes are model compounds for biological systems.

While this work was in progress a paper which reported indium porphyrinates containing a metal–metal bond was published [1]. Now we report the first example of transition metalloporphyrins containing a metal–metal bond.

The synthesis has been achieved by means of different procedures.

$TPPRhMn(CO)_5$ (**1**) and $TPPRhCo(CO)_4$ (**2**) were synthesized by reaction of metalate carbonyl anions and RhTPPCl in THF solution. Good yields were obtained for **1** and the complex was stable in solution, whilst for **2** the yield was lower and the purification procedure lead to extensive decomposition. Yields and stability are in agreement with the reactivity and nucleophilic power of the metalate carbonyl anion and have been previously observed by other authors [1].

$TPPRhSnCl_3$ (**3**) was obtained by reaction of tin(II) dichloride and RhTPPCl in THF solution, while $TPPRhGeCl_3$ (**4**) was synthesized by coupling of a $GeCl_3^-$ salt with RhTPPCl in THF solution. **3** and **4** were stable in solution and recrystallization afforded analytically pure products in high yields.

IR spectroscopic characterization of **1** and **2**, reported in Table I, show absorptions in the carbonyl stretching region. The number and relative intensity

0020-1693/88/$3.50

TABLE I. Spectral Properties of TPPRhML

ML	IR (cm^{-1})	UV (λ_{max} (nm))	NMR (δ (ppm))
$Mn(CO)_5$	2083, 1987	516, 406	8.95 (HPy) 8.31–7.62 (HPh)
$Co(CO)_4$	2055, 2007, 1978	518, 406	9.03 (HPy) 8.40–7.72 (HPh)
$SnCl_3$	345	526, 414	8.90 (HPy) 8.16–7.80 (HPh)
$GeCl_3$	356	526, 418	8.84 (HPy) 8.08–7.75 (HPh)

of these bands are in agreement with those reported in literature [1].

RhTPP seems analogous to InTPP as a ligand and variation from main group to transition metalloporphyrin, as countermoiety in the metal–metal bond, does not significantly affect the carbonyl stretching.

IR data for **3** and **4** are listed in Table I and show characteristic absorptions for $SnCl_3$ and $GeCl_3$ groups at *ca.* 350 cm^{-1}. They are considerably shifted to higher frequency upon coordination if compared to those of the free ions [8, 9]: for instance in $GeCl_3^-$ the absorption falls to 320 cm^{-1}. Such a shift is typical for compounds containing a metal–$M'X_3$ bond and is indicative of an increased oxidation state of M' [10].

UV–Vis spectra agree with five-coordinated RhTPP and absorptions are reported in Table I. In contrast with TPPInML or TPPSnML [1] there are no additional bands in the Soret region, probably due to better stability of the Rh–metal bond toward photodecomposition.

The NMR spectra are not particularly influenced by the change of counterion and are similar to those of RhTPPCl. The pyrrole protons of TPPRhML have a signal at *ca.* 9.00 ppm, analogous to RhTPPCl.

The phenyl protons are equivalent at room temperature in all complexes, and resonances are listed in Table I.

This result is in apparent contrast with the nonequivalence for *ortho* phenyl protons found in other five-coordinated complexes [1], but on the other hand other five-coordinated Rh(III)TPP derivatives show a similar behaviour [11].

Electrochemical, spectroscopic and low temperature NMR studies of PRhML complexes are now in progress to give a more detailed description of the Rh–metal bond.

Acknowledgement

The financial support by MPI (40%) is gratefully acknowledged.

References

1 R. Guilard, P. Mitaine, C. Moise, C. Lecomte, A. Boukhris, C. Swistak, A. Tabard, D. Lacombe, J. L. Cournillon and K. M. Kadish, *Inorg. Chem., 26,* 2467 (1987), and refs. therein.
2 T. Boschi, S. Licoccia and P. Tagliatesta, *Inorg. Chim. Acta, 119,* 191 (1986).
3 T. Boschi, S. Licoccia and P. Tagliatesta, *Inorg. Chim. Acta, 126,* 157 (1987).
4 T. Boschi, S. Licoccia and P. Tagliatesta, *Inorg. Chim. Acta, 143,* 2 (1988).
5 I. A. Cohen and B. C. Chow, *Inorg. Chem., 13,* 488 (1974).
6 T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem., 3,* 104 (1956).
7 G. W. Parshall, *Inorg. Synth., 15,* 222 (1974).
8 M. L. Delwaulle, *C.R., 228,* 1585 (1954).
9 L. A. Woodward and M. J. Taylor, *J. Chem. Soc.,* 407 (1962).
10 D. F. Shriver and M. P. Johnson, *Inorg. Chem., 6,* 1265 (1967).
11 T. Boschi, S. Licoccia, R. Paolesse and P. Tagliatesta, unpublished results from this laboratory.