Ruthenium and Rhodium Carbonyl Tetraphenylporphin Chloride

By EVERYL B. FLEISCHER,* RAY THORP, and DELBERT VENERABLE

(*Department of Chemistry, University of Chicago, Chicago, Illinois* 60637)

WE report the synthesis of two new ruthenium and rhodium porphyrin compounds. Both ruthenium phthalocyanin[1,2] and rhodium porphyrins[3] have been prepared. The preparation of second and third row transition-metal porphyrins *via* the reactive transition-metal carbonyl halides[3] gave two new metal–carbonyl porphyrin compounds. Carbon monoxide was bubbled through a refluxing solution of $RuCl_3$ in EtOH for 3 hr.; tetraphenylporphin (TPP) in glacial acetic acid was added and the mixture was heated for a further 21 hr. The crude ruthenium compound was chromatographed twice on alumina and crystallized from benzene–ethanol. The rhodium compound was prepared by refluxing $[Rh(CO)_2Cl]_2$ with TPP in benzene for 46 hr. and purifiying the crude product as above,† Both of the compounds were characterized as M^{III}CO-TPP-Cl.‡ The compounds both give strong sharp i.r. peaks in the 2000 cm.$^{-1}$ range. The Table gives the i.r. frequency of the carbonyl stretch of the compounds.

The diamagnetic d^6 compounds (Rh^{III}, Ir^{III}, and Fe^{II}) show the expected trend of greater back bonding for the lower oxidation state, as shown by the lower CO stretch for Fe^{II} as compared to the Rh^{III} and Ir^{III}. The Ru^{III} d^5 compound shows a lower stretch than one might expect. The recently prepared $[Ru^{II}(NH_3)_5CO]I_2$ had a carbonyl stretching frequency of 1955 cm.$^{-1}$. The usual CO stretch for the +3 oxidation state of ruthenium as demonstrated in $(NH_4)_2RuCOCl_5$ is 2059 cm.$^{-1}$ and of the +2 oxidation state of $(NH_4)_2RuCO(H_2O)Cl_4$ is 1950 cm.$^{-1}$.

TABLE

Compound	C≡O stretching frequency (cm.$^{-1}$)
Rh^{III}CO-TPP-Cl	2090
Ru^{III}CO-TPP-Cl	1955
Ir^{III}CO-TPP-Cl	2100[3b]
Ir^{III}CO-HPDEE*-Cl	2060[3b]
Fe^{II}CO pyridine PP†	1970[4] 1976[5]

* HPDEE = Hematoporphyrin diethylester

† PP = Protoporphyrindimethyester.

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† This reaction can yield at least three different products: Rh^{III}TPP-Cl, RhCO-TPP-Cl, and Rh-phenyl-TPP-Cl (see ref. 3c).

‡ The compounds gave satisfactory elemental analyses. The visible spectrum in benzene of RhCO-TPP-Cl has λ_{max} at 420 and 532 nm., the RuCO-TPP-Cl at 413 and 528 nm. The RhCO-TPP-Cl is diamagnetic and the RuCO-TPP-Cl is paramagnetic with one unpaired electron (μ_{eff} *ca.* 2·4 BM).

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