Inorganica Chimica Acta, 54 (1981) L211–L212
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Heteropentanuclear Mn_4Rh and Mn_4Ir Complexes with 4,4′-Diisocyanobiphenyl Linkages

AVI EFRATY* and IRENE FEINSTEIN

Department of Organic Chemistry, The Weizmann Institute of Science, Rehovot, Israel

Received June 6, 1981

4,4′-Diisocyanobiphenyl is a nonchelating stereochemically rigid bidentate ligand which undergoes a facile reaction with Rh(1+) and Ir(1+) complexes to afford homonuclear coordination polymers of the type $[M(4,4'\text{-diisocyanobiphenyl})_2^+Cl^-]_n$ [1]. If capable of acting as the linking unit between different transition metal atoms, such as ligand, and alike, could serve as the building blocks of some unusual heteronuclear complexes and polymers. The first step in the development of a synthetic strategy to such materials is described in the current communication.

The reaction of bromomanganesepentacarbonyl with an equimolar quantity of 4,4′-diisocyanobiphenyl in refluxing CH_2Cl_2 for 7 hr gave the monosubstituted product $BrMn(CO)_4$(4,4′-diisocyanobiphenyl) (**1**)– in 50% yield. This complex, containing both coordinated and free isocyanide groups, was characterized by analogy with the previously reported related derivative $BrMn(CO)_4(CNPh)$ [2]. The IR spectrum (CH_2Cl_2) of **1**, in the 1800–2400 cm^{-1} region, consists of bands at 2170 (m), 2138 (s), 2098 (w), 2040 (vs), 2005 (m) and 1935 cm^{-1} (m).

The first two bands were assigned to the coordinated and free isocyanide groups, respectively; whereas the remaining bands of lower frequencies are due to terminal carbonyls. Incidentally, the position of the isocyanide group frequency in the spectrum of the free ligand [3] is found at 2131 cm^{-1}. The carbonyl *trans* to the bromide in the starting manganese-carbonyl complex is expected to be the least susceptible towards exchange, and this may suggest the implication of an equatorial carbonyl group during the course of this substitution reaction.

The presence of a free isocyanide group in **1** makes this complex a potential ligand for further complexation. This feature is of interest from the stand-point of formation of heteronuclear bridged systems. The formation of Rh–Mn and Ir–Mn bridged pentanuclear complexes is exemplified next.

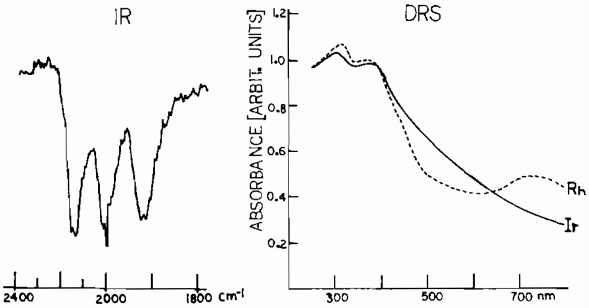
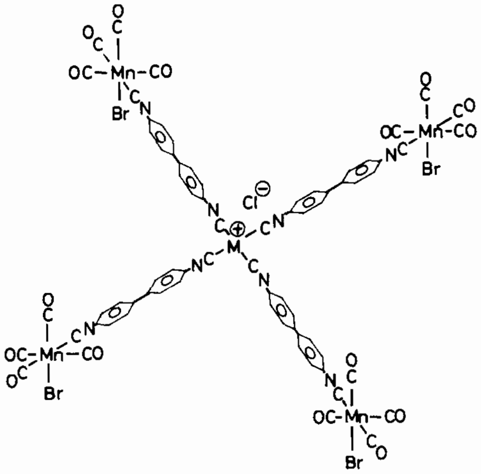


Fig. 1. The IR spectrum (KBr) of **2**; M = Rh in the 1800–2400 cm^{-1} region [left] and the diffuse reflectance spectra (DRS) of **2**; M = Rh, Ir [right].

The reaction $[Rh(CO)_2Cl]_2$ with four-fold molar excess of **1** in CH_2Cl_2 at ambient temperature affords a light–green amorphous precipitate which is analyzed well as $\{Rh[(4,4'\text{-diisocyanobiphenyl})(CO)_4MnBr]_4\}^+Cl^-$ (**2**; M = Rh). A similar reaction with $[IrCl(1,5\text{-cyclooctadiene})]_2$ gave the brown precipitate of **2**; M = Ir. Both reactions proceed quantitatively, and the products are essentially insoluble in either polar or non-polar organic solvents.



The spectroscopic properties of the new complexes appear to be consistent with their formulation as **2**. For instance, the infrared spectrum (KBr) of **2**; M = Rh in the 1800–2400 cm^{-1} region [Fig. 1 (IR)] shows three intense bands which are further split. The high frequency band (2150 cm^{-1}) is in the region of terminally coordinated isocyanides, and its further splitting may be due to the presence of two types of such bands in the complex. The lower frequency bands, centered at 1920 and 2005 cm^{-1}, appear in similar positions to those of the carbonyl stretches in the spectrum of **1**. The further splitting

---

*Author to whom correspondence should be addressed.

of these bands may be due to either solid state effects and/or differences in the relative orientations of the four $BrMn(CO)_4$ moieties in the complex.

The diffuse reflectance spectra of **2**; M = Rh, Ir are shown in Fig. 1 (DRS). The intense and somewhat broad absorptions in the regions 290–325 and 360–380 nm were assigned as $^1A_{1g} \rightarrow {}^1E_u$ and $^1A_{1g} \rightarrow {}^1A_{2u}$ transitions, and this by analogy with the spectral interpretation of some realted $Rh(CNR)_4^+$ cationic systems [4]. A low intensity band centered at 725 nm in the spectrum of **2**; M = Rh may suggest a small degree of oligomerization *via* weak Rh---Rh interactions. In the absence of any distinct bands in the 490–570 nm region, the only reasonable assignment of this band is to a staggered dimer $\{Rh_2[(4,4'\text{-diisocyanobiphenyl})(CO)_4MnBr]_8\}^{2+}\ 2Cl^-$. Assuming the presence of a typical Rh---Rh distance of 3.2 Å, and otherwise idealized bond angles and distances, the separation of the nearest manganese atoms in a staggered dimeric structure is approx. 12.6 Å, and this would imply the absence of steric constrain due to the bulkiness of the $BrMn(CO)_4$ moieties. Contrary to this, the formation of an eclipsed dimeric structure is clearly forbidden on steric grounds.

Similar complexes of the type **2** were also prepared with 1,4-diisocyanobenzene and related ligands.

Acknowledgements

This research programme was supported by a grant received form the N.C.R.D. (Israel) and the K.F.A. (Julich, F.R.G.)

References

1 A. Efraty, I. Feinstein, F. Frolow and L. Wackerle, *J. Am. Chem. Soc., 102,* 6341 (1980).
2 K. K. Joshi, P. L. Pauson, and W. H. Stubbs, *J. Organometal. Chem., 1,* 51 (1963).
3 A. Efraty, I. Feinstein, L. Wackerle and A. Goldman, *J. Org. Chem., 45,* 4059 (1980).
4 K. R. Mann, N. S. Lewis, R. M. Williams, H. B. Gray and J. G. Gordon, II, *Inorg. Chem., 17,* 828 (1978).