*Journal of Organometallic Chemistry,* 433 (1992) C14–C17
Elsevier Sequoia S.A., Lausanne
JOM 22802PC

Preliminary communication

# The *cis*-$\{Re(Ph_2PCH_2CH_2PPh_2)_2\}^+$ metal centre. Synthesis and molecular structure of the dinitrile complex *cis*-$[Re(NCC_6H_4Me\text{-}4)_2(Ph_2PCH_2CH_2PPh_2)_2][BF_4]$

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(Received February 24, 1992)

**Abstract**

Reaction of $NCC_6H_4X$-4 (X = Me, OMe, or Cl) with *trans*-$[ReCl(N_2)(dppe)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$), at room temperature, in the presence of $Tl[BF_4]$, gives the corresponding complexes *cis*-$[Re(NCC_6H_4X\text{-}4)_2(dppe)_2][BF_4]$ (1); the crystal structure of 1 (X = Me) has been determined by single crystal X-ray diffraction analysis.

The electronic factors determining the relative stabilities of the *trans* and *cis* geometrical isomers of octahedral phosphine complexes, particularly of Group VI transition metals with the $\pi$-acceptor ligands CO and $N_2$, have been object of MO theoretical studies [1–3]. These indicate in particular that for 18-electron complexes of the types $[ML_2P_4]$ (M = Cr, Mo, or W; P = monophosphine or 1/2 chelating diphosphine, such as dppe; L = CO [1] or $N_2$ [2,3]), the *cis* isomer should be thermodynamically more stable then the *trans*, although for the corresponding 17-electron compounds an inversion of the relative stability of the isomers should be expected.

Nevertheless, for the related 18-electron Re or Tc complexes listed only the *trans* isomers have been reported: $[MLL'(dppe)_2]^+$ (M = Re [4] or Tc [5]; L and/or L′ = CO, CNR, or NCR); $[MX(dppe)_2]$ (M = Re, X = Cl, L = CO or $N_2$

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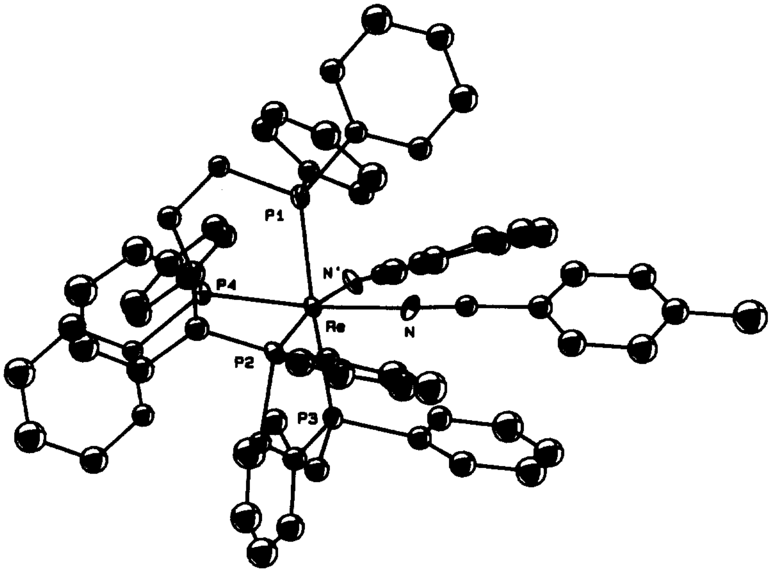

Fig. 1. Molecular structure of the *cis*-$[Re(NCC_6H_4Me\text{-}4)_2(dppe)_2]^+$ moiety. Selected dimensions (with esd's in parentheses): Re–P1 2.375(6), Re–P2 2.368(6), Re–P3 2.384(6), Re–P4 2.368(5), Re–N 2.05(2), Re–N′ 2.08(2), N–C 1.14(2) and N′–C 1.11(2) Å. P1–Re–P2 98.7(2), P1–Re–P3 175.9(2), P2–Re–P3 82.3(2), P4–Re–P1 82.2(2), P4–Re–P2 90.9(2), P4–Re–P3 101.8(2), N′–Re–N 81.6(6), Re–N–C 168(2) and Re–N′–C 170(2)°.

[6], CNR [7a], NCR [7b], or phenylallene [7c] or vinylidene [7d]; M = Tc, X = H, L = CO, $N_2$ [8], or CNR [5b]). They are commonly prepared in refluxing solvents. Similarly, only the *trans* isomers have been obtained for the complexes derived from ligand protonation of the neutral compounds [7b,9], as well as for the dihalo-species $[MX_2(LL)_2]^{n+}$ (M = Re [10a] or Tc [10b]; X = Cl, Br, or F; LL = chelating bis(tertiary phosphine or arsine); $n = 0$ or 1). Therefore, the *trans* geometry of the two diphosphine ligands at the Re or Tc metal centre appears to be favoured for the stabilization of all these 18-, 17- and 16-electron octahedral complexes.

Notwithstanding, we have now succeeded for the first time in the synthesis and structural characterization of complexes with the *cis*-$\{Re(dppe)_2\}^+$ core by treatment at ambient temperature of a THF solution of *trans*-$[ReCl(N_2)(dppe)_2]$ with an organonitrile $NCC_6H_4X\text{-}4$ (X = Me, OMe, or Cl) (*ca.* 2.2 molar equivalents) in the presence of $Tl[BF_4]$ (*ca.* 2 molar equivalents). Under these experimental conditions (which are milder than those in which *trans*-complexes have been obtained), the dinitrile complexes *cis*-$[Re(NCC_6H_4X\text{-}4)_2(dppe)_2][BF_4]$ (**1**) have been isolated as orange crystalline solids. They show $\nu(C\equiv N)$ in the range 2200–2185 $cm^{-1}$, lower by *ca.* 17 to 35 $cm^{-1}$ than those for the free nitriles, consistent with an appreciable $\pi$-electron release from the metal to the nitriles, whereas their $^{31}P\text{-}\{^1H\}$ NMR spectra exhibit two broad resonances [*e.g.*, at $\delta$ −102.4 and −106.7 ppm rel. $P(OMe)_3$, in $(CD_3)_2CO$, for **1**, X = Me].

The molecular structure of **1** (X = Me) has been authenticated by X-ray diffraction analysis and is depicted in Fig. 1, together with selected bond lengths and angles *.

The cation *cis*-$[Re(NCC_6H_4Me\text{-}4)_2(dppe)_2]^+$ shows a distorted octahedral coordination with two linear nitrile ligands (N–C–C angles of 177(2) and 178(2)°), forming an N–Re–N angle of 81.6(6)°, whereas the Re–N and the N–C multiple bond lengths [average 2.065(16) and 1.125(24) Å, respectively] are similar to those exhibited [4b] by *trans*-$[Re(NCC_6H_4Me\text{-}4)_2(dppe)_2]^+$ [2.063(7) and 1.102(13) Å, respectively. However, the average Re–P distance [2.374(6) Å] in the *cis*-isomer appears to be slightly shorter than that of the *trans*, [2.401 Å] [4b], suggesting a stronger $\pi$-electron release from the metal to the phosphines in the *cis* relative to the *trans* arrangement.

Cyclic voltammetry (CV) of complexes **1** at a Pt electrode in 0.2 *M* $[Bu_4N][BF_4]$/THF exhibits a one-electron, reversible oxidation at a potential which is significantly more positive than that displayed by the corresponding *trans* complexes, *e.g.*, $E_{1/2}^{ox} = 0.46$ and 0.33 V *vs* SCE for *cis*-$[Re(NCC_6H_4OMe\text{-}4)_2(dppe)_2]^+$ and *trans*-$[Re(NCC_6H_4OMe\text{-}4)_2(dppe)_2]^+$, respectively, indicating that the HOMO is lower in energy for the *cis* isomer, in agreement with theoretical calculations [1–3] on related complexes. Similarly, the *cis* isomers of the complexes $[M(CO)_2(dppe)_2]$ (M = Cr, Mo or W) are known [11] to be harder to oxidize than the corresponding *trans* isomers. In contrast with the reported electrochemical behaviour of those systems, we did not observe, on the CV time scale, an anodically induced *cis*-to-*trans* isomerization of oxidized complexes **1**. Nevertheless, upon heating complexes **1** in refluxing THF, they convert into the *trans* isomers, which are also isolated when the synthesis is undertaken in refluxing solvents rather than at ambient temperatures.

The lack of redox-induced isomerization has also been noted [12] for $[Mo(N_2)_2(PMe_2Ph)_4]$, the two isomers of which, however, oxidize at the same potential. Moreover, the majority of the bis(dinitrogen) complexes of Cr, Mo and W adopt the *trans* configuration.

It is clear that the relative stabilities of the *cis* and *trans* isomers of octahedral complexes containing unsaturated isoelectronic ligands such as NCR, CNR, CO

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* *Crystal data for* cis-*$[Re(NCC_6H_4Me\text{-}4)_2(dppe)_2][BF_4]\cdot THF$*. $(C_{68}H_{62}N_2P_4Re)(BF_4)\cdot THF$, *M* 4744.1, monoclinic, space group $P2_1/c$ (no. 14), *a* 14.316(3), *b* 25.745(7), *c* 17.340(5) Å, $\beta$ 94.72(2)°, *V* 6370(12) Å$^3$, $Z = 4$, $D_c = 1.237$ g cm$^{-3}$, $F(000) = 2768$, $\mu = 20.4$ cm$^{-1}$, $\lambda = 0.71069$ Å.

All X-ray measurements were made with an Enraf–Nonius CAD-4 diffractometer with graphite-monochromatized Mo-$K_\alpha$ radiation. Cell dimensions and orientation matrices were obtained by least-squares refinement of setting angles for 25 automatically centered reflections with $10 < \theta < 13°$. The intensities of 7904 reflections in the range $1.5 < \theta < 20°$ were measured by the $\omega$–$2\theta$ scan mode. The data were corrected for Lorentz and polarization effects and empirically for absorption.

A total of 5051 independent reflections satisfied the criterion $F > 3\sigma(F)$ and were used for structure solution and refinement. The Re atom was located from a Patterson map, and all the other non hydrogen atoms were found from subsequent difference Fourier syntheses. All hydrogen atoms were included in idealized positions. A disordered model was used to refine the $BF_4$ anion. Least-squares refinements with isotropic thermal parameters for all the C, O and F atoms and anisotropic thermal parameters for Re, P, N and B atoms gave an agreement factor $R = 0.074$. All computations required to solve and refine the structure were made with SHELX76 [14], drawings were made with ORTEP-II [15]. Full lists of structure factors, atomic coordinates, and bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre.

and $N_2$ are determined by a delicate balance of factors, including the electronic properties of the metal and of all the ligands, and thus generalizations must be taken cautiously. Our results do not accord entirely with theoretical schemes [1–3] for related species. We have demonstrated the formation of the previously unknown *cis*-$\{Re(dppe)_2\}^+$ and its conversion into the *trans* isomer. The synthetic implications of these observations are under investigation. Complexes **1** are rare examples [5] of complexes with more than one nitrile bound at an electron-rich centre with no stabilization by stronger $\pi$-acids such as CO in $[M(CO)_{6-n}(NCMe)_n]$ (M = Cr, Mo, or W; $n$ = 1–3) [13].

**Acknowledgements.** We thank JNICT, under projects PMCT/C/CEN/339 and 367/90 and Grants BD/135/90 RM and BD/BIC 169/90 RM, and INIC (Portugal) for partial support of this work, as well as Dr. R.L. Richards (AFRC, Nitrogen Fixation Laboratory, UK) for stimulating discussions.

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