

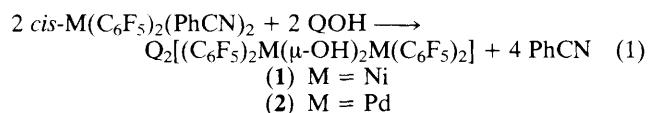
Synthesis of Hydroxo-organo-complexes of the Nickel Group Elements

Gregorio López,* Gabriel García, José Ruiz, Gregorio Sánchez, Joaquín García, and Consuelo Vicente

Departamento de Química Inorgánica, Universidad de Murcia, Espinardo-Murcia, Spain

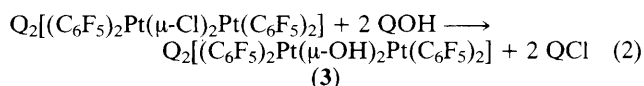
The considerable nucleophilicity of the OH bridges in the new hydroxo complexes $[(C_6F_5)_2M(\mu-OH)_2M(C_6F_5)_2]^{2-}$ ($M = Ni, Pd, Pt$) is indicated by high field proton resonances and the formation of μ -pyrazolate derivatives from $[(C_6F_5)_2Ni(\mu-OH)_2Ni(C_6F_5)_2]^{2-}$.

No binuclear anionic species of the general type $[R_2M(\mu-OH)_2MR_2]^{2-}$ ($R =$ alkyl or aryl) are known for the nickel group. The complexes $Q_2[(C_6F_5)_2M(\mu-OH)_2M(C_6F_5)_2]$ ($Q = NBu_4$; $M = Ni, Pd$) have now been prepared by reaction of the corresponding *cis*- $M(C_6F_5)_2(PhCN)_2$ † with 20% aqueous QOH [equation (1)] and isolated by the addition of water to the reaction medium. However, the platinum analogue could not be obtained from the corresponding benzonitrile adduct, *cis*- $Pt(C_6F_5)_2(PhCN)_2$, because, instead of the displacement reaction, the co-ordinated nitrile underwent the alternative solvolysis reactions known for this type of compound.‡ Complex (3) was prepared by reaction between the chloro-bridged anion² $[(C_6F_5)_2Pt(\mu-Cl)_2Pt(C_6F_5)_2]^{2-}$ and 20% QOH_(aq) in acetone [equation (2)], the compound being precipitated by addition of water.

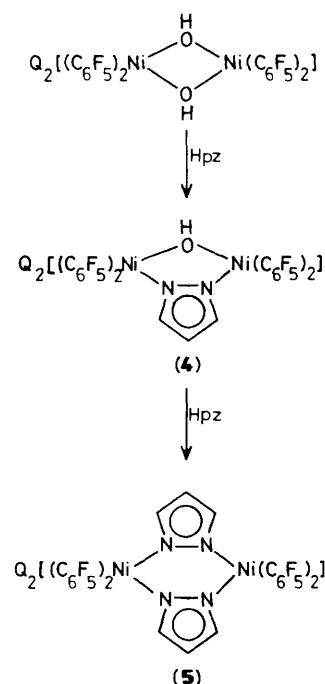


† The synthesis of *cis*- $Pd(C_6F_5)_2(PhCN)_2$ has been described elsewhere [C. de Haro, G. García, G. Sánchez, and G. López, *J. Chem. Res.*, 1986, (S) 11; (M) 1128]. The nickel and platinum analogues were prepared from $NiBr_2$ and $PtCl_2$ by a similar procedure. *cis*- $Ni(C_6F_5)_2(PhCN)_2$: m.p. 145 °C (decomp.); i.r. 2290, 2280 ($\nu C\equiv N$), 790 sh, 785 (*X*-sensitive mode of C_6F_5) cm^{-1} ; 1H n.m.r. ($[^2H_6]$ acetone) δ 7.7 (m, C_6H_5); ^{19}F n.m.r. ($[^2H_6]$ acetone) δ -116.3 (d, 4 F_o , $J_{o,m}$ 25.4 Hz), -161.5 (t, 2 F_p , $J_{p,m}$ 19.4 Hz), and -164.7 (m, 4 F_m). *cis*- $Pt(C_6F_5)_2(PhCN)_2$: m.p. 238 °C (decomp.); i.r. 2265, 2258 ($\nu C\equiv N$), 810, 800 (*X*-sensitive mode of C_6F_5); 1H n.m.r. ($CDCl_3$) δ 7.62 (m, C_6H_5); ^{19}F n.m.r. ($CDCl_3$) δ -121.1 (m, 4 F_o , J_{PtF} 480 Hz), -162.0 (m, 2 F_p), -165.2 (m, 4 F_m).

‡ I.r., 1H n.m.r., and mass spectrometry data showed that the ligands $PhC(=O)NH^-$ or $PhC(OMe)=NH$ were present in the isolated solids, where the solvent used was acetone-water or methanol-water, respectively.



The three hydroxo-complexes were obtained in high yields and the conductivity studies in acetone at different concentrations afforded values of *A* in Onsager's equation supporting



Scheme 1

Table 1. Data for compounds $(\text{NBu}_4)_2[(\text{C}_6\text{F}_5)_2\text{M}(\mu\text{-OH})_2\text{M}(\text{C}_6\text{F}_5)_2]$.

M	Colour	M.p./°C (decomp.)	δ (^1H)	δ (^{19}F) ^b	I.r. $\nu(\text{OH})$ /cm ⁻¹
Ni	Orange	217	-5.74 (s, 2H, OH)	-114.5 (d, 8F _o , J _{o,m} 28.5 Hz) -167.2 (t, 4F _p , J _{p,m} 19.4 Hz) -168.6 (m, BF _m)	3620
Pd	White	180	-2.84 (s, 2H, OH)	-115.6 (d, BF _o , J _{o,m} 27.3 Hz) -164.9 (t, 4F _p , J _{p,m} 20.1 Hz) -166.4 (m, 8F _m)	3610
Pt	White	265	-1.21 (s, 2H, OH)	-121.8 (d, 8F _o , J _{o,m} 25.1, J _{Pt,F} 534 Hz) -167.1 (m, 12F _{m+p})	3600

^a For all three compounds additional peaks due to $(\text{NBu}_4)^+$ are found at δ 3.32 (t, 16H, NCH, J_{HH} 7.1 Hz), 1.61 (m, 32H, -CH₂-CH₂-), and 0.97 (t, 24H, CH₃, J_{HH} 6.24 Hz). ^b In p.p.m. vs. CFC1₃.

their dinuclear nature.³ Their i.r. spectra showed the bands attributed to the C₆F₅ group⁴ and a split band at ca. 800 cm⁻¹ due to the *cis*-M(C₆F₅)₂ fragment.⁵ Some relevant data are collected in Table 1.

The considerable nucleophilicity of the OH bridges in complexes (1)–(3) is indicated by the high field proton resonances, which are similar to those reported for other compounds containing M–OH bonds (M = Ni, Pd, Pt),^{6,7} and the chemical reactivity exhibited by complex (1) towards pyrazole (Hpz). Complexes containing both μ -pz and μ -OH have been isolated or detected in the reaction of Hpz with $[(\text{C}_5\text{Me}_5)_2\text{M}(\mu\text{-OH})_2\text{M}(\text{C}_5\text{Me}_5)_2]^+$ (M = Rh or Ir).⁸ We have isolated complexes (4) and (5) by the reaction of (1) with pyrazole in the appropriate molar ratio in acetone (Scheme 1). § Presumably complexes (4) and (5) are formed by protonation by Hpz of (1) and (4), respectively, to form

aqua-intermediates, which react with $(\text{pz})^-$ to give the μ -pyrazolate complexes.

The authors thank DGICYT (project PB87-0690), Spain, for financial support and Comunidad Autónoma de Murcia, (Consejería de Cultura, Educación y Turismo) for grants (to J. G. and C. V.).

Received, 11th February 1989; Com. 9/00667B

References

- M. Wada and T. Shimohigashi, *Inorg. Chem.*, 1976, **15**, 954, and references therein.
- R. Usón, J. Forniés, M. Tomás, and R. Fandos, *J. Organomet. Chem.*, 1984, **263**, 253.
- R. D. Feltham and R. G. Hayter, *J. Chem. Soc.*, 1964, 4587.
- D. A. Long and D. Steel, *Spectrochim. Acta*, 1963, **19**, 1955.
- R. Usón, J. Forniés, F. Martínez, and M. Tomás, *J. Chem. Soc., Dalton Trans.*, 1980, 888.
- E. Carmona, J. M. Marín, M. Paneque, and M. L. Poveda, *Organometallics*, 1987, **6**, 1757.
- H. E. Bryndza, L. K. Fong, R. A. Paciello, W. Tam, and J. E. Bercaw, *J. Am. Chem. Soc.*, 1987, **109**, 1444, and references cited therein.
- D. Carmona, L. A. Oro, M. P. Lamata, M. P. Puebla, J. Ruiz, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1987, 639, and references cited therein.

§ Both compounds were obtained as yellow crystals which gave satisfactory elemental analyses and molar conductance data. For (4): m.p. 178 °C; ^1H n.m.r. ($[\text{D}_6]\text{acetone}$) δ -4.24 (s, 1H, μ -OH), 5.50 (t, 2H, C–CH–C, J 1.95 Hz), 6.01 (d, 2H, N–CH–C); i.r. (cm⁻¹) 3600 (ν OH). For (5) m.p. 242 °C; ^1H n.m.r. ($[\text{D}_6]\text{acetone}$) δ 5.48 (t, 2H, C–CH–C, J 1.83 Hz), 6.95 (d, 4H, N–CH–C).