ELECTRONIC SUPPLEMENTARY INFORMATION

Title: Pentamethylcyclopentadienyl Osmium Complexes that Contain Diazoalkane, Dioxygen and Allenylidene Ligands: Preparation and Reactivity

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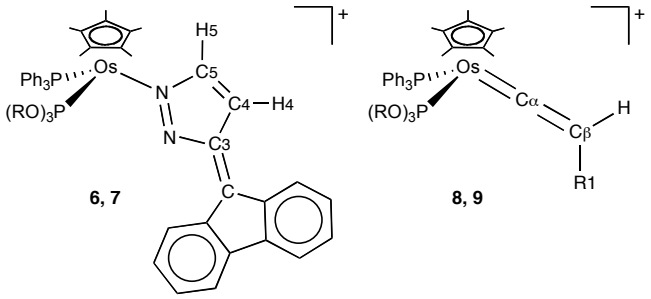

The ^{1}H NMR spectra of the 3*H*-pyrazole complexes [Os(η^5-C_5Me_5)(η^1-N=CC($C_{12}H_8$)CH=CH)(PPh_3){$P(OR)_3$}]BPh_4 (**6, 7**) showed two doublets at 7.53 and 6.72 ppm (J_{HH} = 2.8 Hz) for **6** and at 7.87 and 6.73 ppm (J_{HH} = 3.0 Hz) for **7** attributed to H5 and H4 of the heterocycle, and the characteristic signals of the $C_{12}H_8$ substituent at C3. The ^{13}C{^{1}H} NMR spectra confirmed the presence of the 3*H*-pyrazole ligand showing, for **6**, two singlets at 158.13 and 139.39 ppm which, in a HMQC experiment, were correlated with the doublets at 7.53 and 6.72 ppm observed in the proton spectrum and attributed to C5 and C4 carbon resonances of the heterocycle; a singlet at 105.38 ppm was attributed to C3. In the ^{13}C{^{1}H} NMR spectrum of **7**, two singlets appeared at 157.47 and 139.50 ppm which, in a HMQC experiment, were correlated with the doublets at 7.87 and 6.73 ppm observed in the proton spectrum and attributed to C5 and C4 carbon resonances of the heterocycle. In the spectra, the signals of the ancillary ligands and the BPh_4 anion also appeared. The ^{31}P spectra are doublets of doublets fitting the proposed formulation for the complexes.

The IR spectra of vinylidene complexes **8** and **9** showed a medium-intensity band at 1662–1604 cm^{-1} attributed to the $\nu_{Os=C=C}$ of the vinylidene ligand. Its presence was confirmed by the multiplet taht appeared at 3.15 for **8b**, 3.13 for **8c,** 2.83 for **8d** and 3.15 ppm for **9c** in the proton

NMR spectra and attributed to the =C(H)R vinylidene proton. The $^{13}C\{^{1}H\}$ NMR spectra showed a doublet of doublets at 316.31 for **8b**, 317.46 for **8c,** 310.99 for **8d** and 327.17 ppm for **9c** of the Cα carbene carbon resonance =Cα=Cβ(H)[1-4] and a singlet at 115.69 for **8b**, 115.53 for **8c,** 107.47 for **8d** and 115.42 ppm for **9c** which, in a HMQC experiment, was correlated with the multiplet between 3.15 and 2.83 ppm in the ^{1}H NMR spectra and attributed to the Cβ carbon resonance of the =C=C(H)R1 group. The ^{31}P NMR spectra appeared as two doublets in agreement with the proposed formulation for the complexes.

References

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