

Synthesis and characterization of iridium(III) complexes containing Tp^{Me_2} and acac ligands and their reactivity with electrophiles

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Experimental section

General methods

All preparations and manipulations were carried out under nitrogen or argon atmosphere following conventional Schlenk techniques. Complex (**1**) was synthesized as reported in the literature.¹ Solvents were dried rigorously and degassed before use. The prepared compounds were purified by flash column chromatography, through silica gel (Merck 60, 230-400 mesh). Microanalyses were recorded on a Perkin Elmer Series II 2400 apparatus. Infrared spectra were recorded on a PERKIN Elmer 2000 FT-IR instrument in KBr, and NMR spectra on a JEOL Eclipse 400 spectrometer using CDCl₃ as the solvent. The ¹H and ¹³C residual resonance signals of the solvent were used as internal standards, but chemical shifts are reported with respect to TMS. Most of the NMR assignments are based on extensive ¹H-¹H decoupling experiments, and homo and heteronuclear two-dimensional spectra. All minima and transition states were localized with the deMon2k software² using the ADFT method at the VWN/DZVP/GEN-A2 + SDD level of theory. For the variational fitting of the density, automatically generated auxiliary functions were employed. Optimizations were performed with a quasi-Newton trust region method using analytic gradients. Frequency analysis was performed to characterize all relevant intermediaries. Second derivatives were calculated through numerical differentiation of the analytic gradients. Location of transition states was performed using the double-ended saddle interpolation method³ as implemented in the deMon2k software. Gibbs free energies were calculated with the Gaussian 09 software⁴ using the DFT method at the PBE/6-31G* + SDD level of theory. All thermodynamic properties were calculated at 343.15 K (70 °C). X-Ray diffraction analyses for **6**, **8** and **9** were collected in an Agilent Gemini Diffractometer using Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). Data were integrated, scaled, sorted, and averaged using the CrysAlisPro software package. The structures we solved using direct methods, using SHELX 97⁵ and refined by full matrix least squares against F².⁶ All non hydrogen atoms were refined anisotropically. The position of the hydrogen atoms were kept fixed with common isotropic display parameters.

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