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Preliminary communication

ortho-METALATION OF FERROCENE

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Summary

The first example of intramolecular *ortho*-metalation of a metallocene by a transition metal is described.

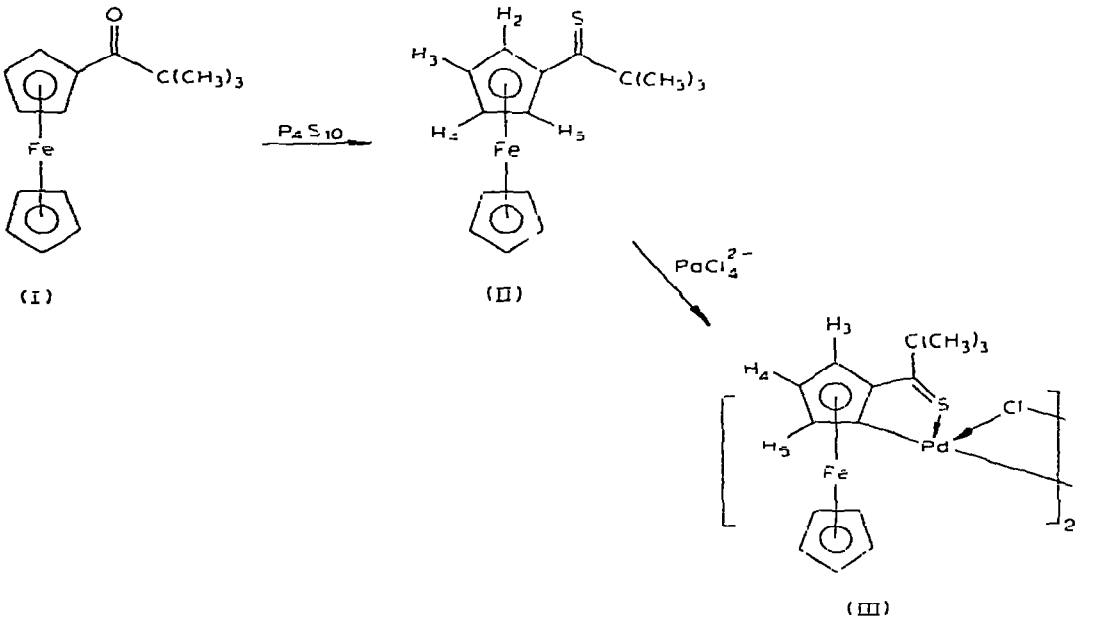
There has been considerable interest in recent years in the intramolecular *ortho*-metalation of nitrogen, phosphorus, and sulfur donor ligands by transition metals [1]. Although numerous *ortho*-metalated complexes have been prepared, none involve intramolecular metalation of a metallocene. At least one unsuccessful attempt to synthesize such a complex (i.e., of a ferrocene derivative) has been reported in the literature [2]. This communication reports the first example of a transition metal *ortho*-metalated ferrocene.

Thiopivaloylferrocene (II)*, a purple oil [IR(neat) ν(CS) 1243 cm^{-1}; NMR ($CDCl_3$) δ 1.47 (s, 9H, $C(CH_3)_3$), δ 4.10 (s, 5H, C_5H_5), δ 4.63 (t, 2H, $H_{3,4}$), δ 5.09 (t, 2H, $H_{2,5}$)], was obtained in 78% yield by treating pivaloylferrocene (I) with P_4S_{10} and $NaHCO_3$ in diglyme for 21 h at room temperature [3]. Treatment of the thioketone II with an equimolar amount of sodium tetrachloropalladate in methanol afforded the deep green *ortho*-metallated complex III [m.p. 220° (dec.)] in 62% yield.

The molecular weight of III (osmometry), was 839, in good agreement with the calculated value of 856. The thiocarbonyl stretching absorption (1222 cm^{-1}) occurred at lower wave number than that observed for II. The NMR spectrum ($CDCl_3$) of the cyclopalladated complex is consistent with the assigned structure showing single proton absorptions at δ 5.13, 4.73, and 5.77, due to H_3, H_4, and H_5 respectively, as well as singlets at δ 1.43 (9H, $C(CH_3)_3$) and at δ 4.45 (5H, C_5H_5).

The simple synthesis of complexes of structural type III should provide an entry into novel metallocene chemistry.

*Satisfactory (± 0.4%) C, H, S, Fe, Pd, Cl analyses were obtained for the new compounds.



(I) (II) (III)

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References

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