

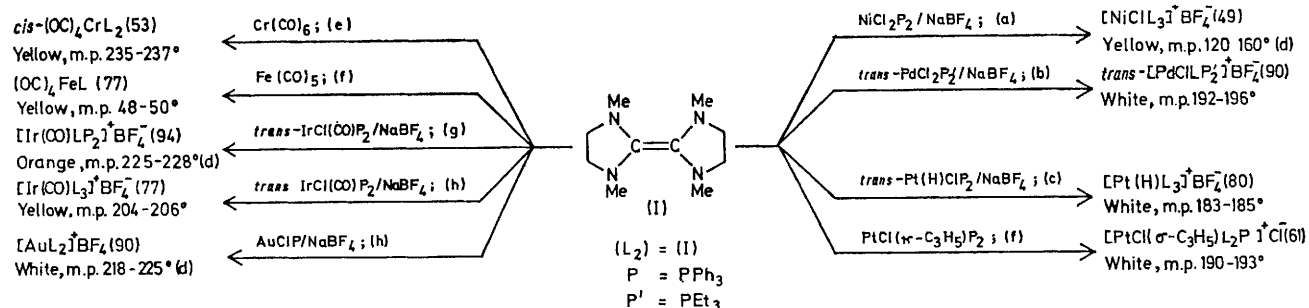
## A General Synthesis of Transition-metal Carbene Complexes: Cr<sup>0</sup>, Fe<sup>0</sup>, Ir<sup>I</sup>, Ni<sup>II</sup>, Pd<sup>II</sup>, Pt<sup>II</sup>, and Au<sup>I</sup> Mono- and Oligo-carbene Species from Electron-rich Olefins

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**Summary** A general method of synthesis of transition-metal carbene complexes involves displacement of CO, olefin, tertiary phosphine, or hal<sup>-</sup> from a suitable metal precursor by a nucleophilic carbene fragment derived from an electron-rich olefin; the latter appear to be comparable in their transition metal reactivity to tertiary phosphines.

No general synthetic route to transition-metal carbene complexes has hitherto been available.<sup>1</sup> We have pre-

(see Scheme). This involves displacement of neutral ligands CO, olefin, or tertiary phosphine, or the anionic hal<sup>-</sup>. The Scheme demonstrates *inter alia* the first reports of (i) carbene complexes of Ir<sup>I</sup> and Ni<sup>II</sup>, (ii) a range of di- and tri-carbene complexes (of Cr<sup>0</sup>, Ir<sup>I</sup>, Ni<sup>II</sup>, Pd<sup>II</sup>, Pt<sup>II</sup>, and Au<sup>I</sup>,† and (iii) the probability that 'transfer' reactions involve electron-rich olefins as intermediates [*e.g.*,  $\pi$ -C<sub>8</sub>H<sub>5</sub>Mo(CO)(NO){C(OMe)Ph} + Fe(CO)<sub>5</sub>  $\xrightarrow{h\nu}$  (OC)<sub>4</sub>Fe-C(OMe)Ph +  $\pi$ -C<sub>5</sub>H<sub>5</sub>Mo(CO)<sub>2</sub>NO].<sup>3</sup> Complete analytical and spectroscopic data are available for all compounds in the Scheme.



SCHEME. Typical transition metal complex reactions of an electron-rich olefin (yields, %, in parentheses).

Reaction conditions: (a) 40–50°, 1 h, PhMe, (b) 90–100°, 10 min, PhMe, (c) 110°, 3 h, PhMe, (d) 110°, 7 h, PhMe, (e) 20°, 8 h, *hν*, THF, (f) 80°, 1 h, PhH, (g) 56°, 3 h, Me<sub>2</sub>CO, (h) 110°, 15 min, PhMe.

viously reported that an electron-rich olefin splits the dihalide-bridge of binuclear Pd<sup>II</sup> or Pt<sup>II</sup> complexes such as Pt<sub>2</sub>Cl<sub>4</sub>(PEt<sub>3</sub>)<sub>2</sub>;<sup>2</sup> and we now show that electron-rich olefins, *e.g.*, (I), provide a widely applicable synthetic procedure

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† A tetra- (Pt<sup>II</sup>) and some di- (Cr<sup>0</sup>, W<sup>0</sup>, Fe<sup>II</sup>, Pd<sup>II</sup>, Pt<sup>II</sup>, and Hg<sup>II</sup>) carbene complexes are known<sup>1a</sup>.

<sup>1</sup> (a) *Cf.*, D. J. Cardin, B. Cetinkaya, and M. F. Lappert, *Chem. Rev.*, 1972, **72**, 545; (b) F. A. Cotton and C. M. Lukehart, *Progr. Inorg. Chem.*, 1972, **16**, 487.

<sup>2</sup> D. J. Cardin, B. Cetinkaya, M. F. Lappert, Lj. Manojlović-Muir, and K. W. Muir, *Chem. Comm.*, 1971, 400; D. J. Cardin, B. Cetinkaya, E. Cetinkaya, M. F. Lappert, Lj. Manojlović-Muir, and K. W. Muir, *J. Organometallic Chem.*, 1972, **44**, C59.

<sup>3</sup> E. O. Fischer, H. J. Beck, C. G. Kreiter, J. Lynch, J. Müller, and E. Winkler, *Chem. Ber.*, 1972, **105**, 162.