Electron-Rich Olefins as Heteroatom Donors; the Crystal and Molecular Structures of μ-Dimethylthioethene-1,1-dithiolato-*SS'S''S'''*-bis[chloro(triethylphosphine)-platinum(II)] and Tetracarbonyl-*NN'N''N'''*-tetramethylbi(imidazolidin-2-ylidene)-*NN''*-chromium(0)

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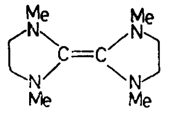
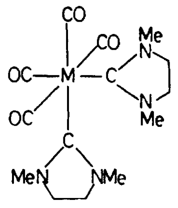
Summary. Electron-rich olefins like $[\overline{\mathrm{MeN(CH_2)_\mathit{n}N(Me)}}\mathrm{C}]_2$ yield *NN''*-bonded complexes, such as the Cr title compound, which thermolyse (for $n = 2$ more readily than for $n = 3$) to give carbene-metal complexes; acyclic olefins like $C_2(SMe)_4$ may afford similar chelate complexes which, however, are not carbene-metal precursors, although Me–S cleavage may occur, for example, to give the diplatinum title compound.

We have previously shown that electron-rich olefins, *e.g.*, (I), have an extensive carbene-ligand transition metal chemistry, yielding complexes such as (II; M = Cr), but the reaction pathway to such compounds has remained obscure.[1] We now describe an alternative mode of interaction between an electron-rich olefin and a suitable transition metal substrate, yielding a complex in which the olefin acts as a heteroatom donor. For a cyclic olefin, *e.g.*, (I) or (III), these complexes are isolated under milder conditions than those required for formation of carbene-metal derivatives, and indeed they are converted into the latter upon thermolysis. For acyclic olefins such as (IV) or (V), more severe reaction conditions are required for the formation of *NN''*- or *SS''*-metal adducts, *e.g.*, $[\mathrm{Cr\{C_2(SMe)_4\}(CO)_4}]$, which we have been unable to transform into carbene-metal products.


(I)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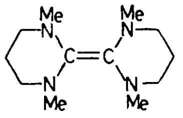
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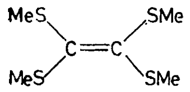
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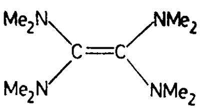
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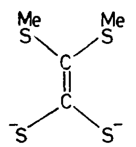
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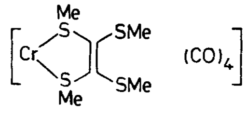
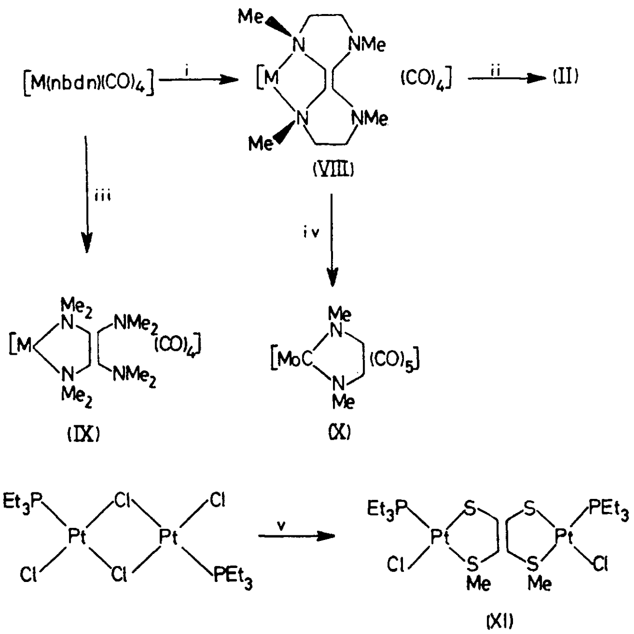

(VII)

It is possible that C–C cleavage requires electron transfer from metal *d*-orbitals into π*-orbitals of the *NN''*-olefin complex (VII) in a vibrationally excited state (*cf.*, *X*-ray data, below) and that a suitable conformation is governed by the nature and size of the heterocyclic organic rings; such effects do not significantly influence the molecular orbital energy levels in the free olefins.[2] Thus, whereas formation of the complexes homologous with (VIII) was possible from the six-membered heterocycle (III), conversion into a carbene-metal complex (and then merely the monocarbene product) occurred less readily under similar mild conditions (Scheme).



nbdn = norbornadiene

Scheme. Reagents and conditions: i, (I), PhMe–Et_2O, 20 °C (M = Cr, Mo, or W); ii, 140 °C, no solvent (smooth transition by differential scanning calorimetry for M = Mo); first-order rate law; iii, (V), 110 °C, PhMe, 1–2 h; iv, PhMe, 110 °C, 15 min (M = Mo); v, (IV), xylene, 140 °C, 20 min.

For the compound (IV), a further reaction has been observed, whereby Me–S fission accompanies metal-sulphur bond formation; the ligand is thus the tetradentate dianion (VI), which may be regarded as an intermediate between the potentially tetra-*S*-dentate compound (IV) and the as yet unknown bridging bis(dithiolate), $C_2(S^-)_4$. The structures of the new metal complexes have been established by analytical and spectroscopic (i.r., ^{1}H and ^{13}C n.m.r., and mass spectrometry) methods and, in two cases, by single crystal *X*-ray diffraction. Their chemical features are further illustrated in the Scheme and the Table. The

TABLE. Selected data on some transition metal complexes derived from electron-rich olefins

Compound	ν(CO)/cm^{-1} (THF or toluene solution)	^{13}C N.m.r. (p.p.m. rel. to Me_4Si, in C_6D_6 or $CDCl_3$) olefinic C	mutually *cis*-$(CO)_2$	mutually *trans*-$(CO)_2$	ring (CH_2)'s	Me
(II; M = Mo)[a]	1994, 1868, 1863, 1838	222·9	219·4	211·5	51·7	38·8
(VIII; M = Mo)	2005, 1895, 1870, 1835	134·6	222·4	206·6, 206·8	51·0, 62·7[b]	38·65, 52·7[b]
(VIII; M = W)	2010, 1895, 1875, 1830	—	—	—	—	—
(IX; M = Mo)	—	148·0	222·6	206·8	—	45·1, 47·0[b]
(X; M = Mo)[a]	2064, 1931	215·4	(212·5)[c]	(207·4)[d]	51·2	38·8
(VII)	2005, 1885, 1865, 1840	141·6	227·0	215·9	—	17·7, 29·5[b]

[a] $\nu(CN_2)$, *ca.* 1500 cm^{-1}. [b] Donor atom substituent. [c] CO *trans* to C_{carb}. [d] Four equivalent CO's.

compound (XI) has m.p. 230—232 °C and ν(PtCl) 318 and 296 cm^{-1}.

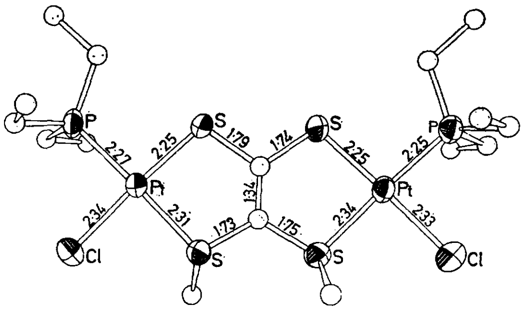


FIGURE 1. *X*-Ray structure of (XI)

Crystal data (measured on a Hilger and Watts Y290 diffractometer using monochromated Mo-K_α *X*-rays): (a) $C_{16}H_{36}Cl_2P_2Pt_2S_4$, *M* 879·8, monoclinic, space group *Cc*, $a = 7{\cdot}552(2)$, $b = 30{\cdot}193(6)$, $c = 12{\cdot}078(2)$ Å; $\beta = 96{\cdot}70(2)°$; $Z = 4$; $R = 0{\cdot}032$ for 1061 independent reflections. E.s.d.'s on bond lengths (Figure 1) are 0·01 Å for bonds to Pt and 0·04 Å otherwise. The complex has approximate C_2 molecular symmetry with the Pt, S, P, and Cl atoms coplanar and bond lengths and angles normal. The difference of 0·09 Å between the two non-equivalent Pt–S bond lengths is pscribed mainly to the greater *trans*-influence of the phosahine ligands. The distance of the double bond from Pt atoms is 3·1 Å and any direct interaction with the π-orbital of the double bond is likely to be small.

(b) $C_{14}H_{20}CrN_4O_4$, *M* 360·3, monoclinic, space group $P2_1/c$, $a = 9{\cdot}888(2)$, $b = 15{\cdot}806(3)$, $c = 12{\cdot}382(2)$ Å; $\beta = 118{\cdot}87(2)°$; $Z = 4$; $R = 0{\cdot}034$ for 1225 independent reflections. E.s.d.'s on bond lengths (Figure 2) are 0·01 Å. The two nitrogen atoms involved in bonding to the chromium atom are tetrahedral with normal bond lengths; the other two, however, have systematically shorter bonds and larger bond angles indicating a hybridisation nearer to sp^2, which indicates interaction of the lone pair *p*-orbital on each nitrogen with the double bond π-orbital. The two *trans* carbonyl groups competing for π-bonding with the Cr atom have longer Cr–C bonds than the other two and, in addition, are significantly bent away from the electron-rich olefin, presumably for steric reasons. Similar effects have been seen in the structure of $[Mo(CO)_4(Ph_2PCH_2PPh_2)]$.[3] The double bond is at a distance of 2·9 Å from the chromium atom and any direct interaction is unlikely.

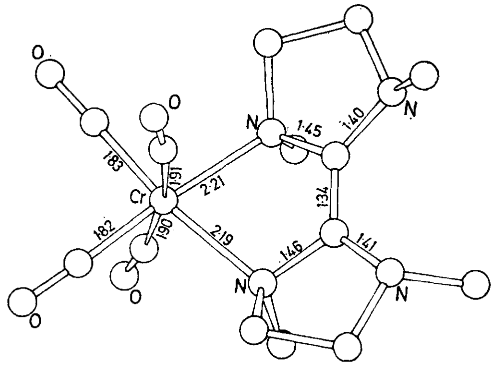


FIGURE 2. *X*-Ray structure of (VIII; M=Cr)

We thank the S.R.C. for support and Professor R. Mason for provision of *X*-ray facilities.

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[1] B. Çetinkaya, P. Dixneuf, and M. F. Lappert, *J.C.S. Dalton*, 1974, 1827; and references therein.

[2] B. Çetinkaya, G. H. King, S. S. Krishnamurthy, M. F. Lappert, and J. B. Pedley, *Chem. Comm.*, 1971, 1370.

[3] K. K. Cheung, T. F. Lai, and K. S. Mok, *J. Chem. Soc.* (*A*), 1971, 1644.