JOURNAL OF THE CHEMICAL SOCIETY

Chemical Communications

Number 23
1988

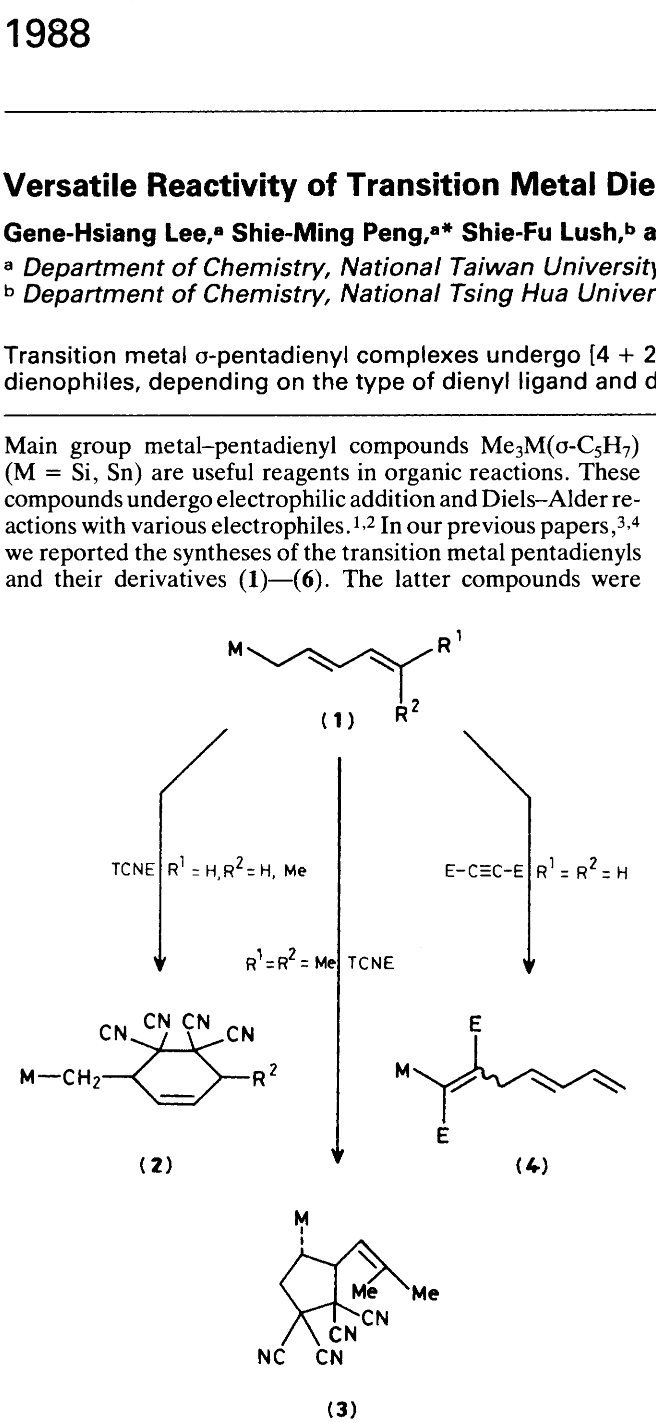
Versatile Reactivity of Transition Metal Dienyl Ligands with Dienophiles

Gene-Hsiang Lee,[a] Shie-Ming Peng,[a]* Shie-Fu Lush,[b] and Rai-Shung Liu[b]*

[a] *Department of Chemistry, National Taiwan University, Taipei, Taiwan, Republic of China*
[b] *Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 30043, Republic of China*

Transition metal σ-pentadienyl complexes undergo [4 + 2] and [3 + 2] cycloadditions and insertion reactions with dienophiles, depending on the type of dienyl ligand and dienophile.

Main group metal–pentadienyl compounds $Me_3M(\sigma\text{-}C_5H_7)$ (M = Si, Sn) are useful reagents in organic reactions. These compounds undergo electrophilic addition and Diels–Alder reactions with various electrophiles.[1,2] In our previous papers,[3,4] we reported the syntheses of the transition metal pentadienyls and their derivatives (**1**)—(**6**). The latter compounds were shown to undergo electrophilic addition, possible at the γ and ε carbons of the dienyl ligand.[5] In this paper, we report the preliminary results of their reaction chemistry with reactive dienophiles. As depicted in Scheme 1, their reaction pathways vary with the nature of the dienophiles and dienyl ligands.



M=CpMo(CO)$_3$
a; R^1=R^2=H
c; R^1=Me, R^2=H
e; R^1=R^2=Me

M=CpFe(CO)$_2$
b; R^1=R^2=H
d; R^1=Me, R^2=H
f; R^1=R^2=Me

Scheme 1. E = CF_3 or CO_2Me (Cp = C_5H_5).

Addition of tetracyanoethylene (TCNE) to an equimolar quantity of compounds (**1a—c,e,f**) in dichloromethane at 23 °C over 4 h led to the 1 : 1 adducts (**2a—c,e,f**) in high yields (>45%). Analytically pure yellow crystals were obtained after crystallization from CH_2Cl_2–hexane.† The reaction of (**1d**) with TCNE failed to give analogous crystals, giving instead a blue solid of undetermined composition. The ^1H and ^{13}C n.m.r. spectra reveal that these adducts consist of two classes of structures. A [4 + 2]cycloaddition is assignable to adducts (**2a—c**) and a [3 + 2]cycloaddition is assignable to (**3e,f**). An *X*-ray diffraction study was undertaken of the representative complexes $CpFe(CO)_2(CH_2CHC(CN)_2C(CN)_2CH{=}CH)$ (**2b**) and $CpMo(CO)_3[CHCH(CH{=}CMe_2)C(CN)_2C(CN)_2CH_2]$ (**3e**).‡ It is evident from the ORTEP diagram that the

---

† Satisfactory analytical and/or spectroscopic data were obtained for all new compounds.

‡ *Crystal data* for (**2b**): $C_{18}H_{12}N_4FeO_2$, orthorhombic, space group $Pca2_1$, a = 13.174(2), b = 10.601(2), c = 12.315(3) Å, Z = 4, U = 1720(2) Å^3, D_c = 1.437 g cm^{-3}, $F(000)$ = 755.81, λ(Mo-K_α) = 0.7093 Å, crystal dimensions 0.45 × 0.50 × 1.00 mm, R = 0.043, R_w = 0.030 for 1556 unique data with $I > 3\sigma(I)$ and 227 variables. Data were collected on an Enraf-Nonius CAD-4 diffractometer. The structure was solved by the Patterson method. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were added at idealized positions and included in the structure factor calculations.

For (**3e**): $C_{21}H_{16}MoO_4N_4$, monoclinic, space group $P2_1/n$, a = 10.760(8), b = 15.898(6), c = 12.57(4) Å, β = 96.97(14)°, Z = 4, U = 2134(1) Å^3, D_c = 1.457 g cm^{-3}, $F(000)$ = 943.66, λ(Mo-K_α) = 0.7093 Å, crystal dimensions 0.5 × 0.6 × 0.12 mm, R = 0.039, R_w = 0.043, for 2898 unique data with $I > 3\sigma(I)$ and 263 variables. Data were collected on an Enraf-Nonius CAD-4 diffractometer. The structure was solved by the Patterson method. All non-hydrogen atoms were refined with anisotropic parameters. All hydrogen atoms were added at idealized positions and included in the structure factor calculations. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

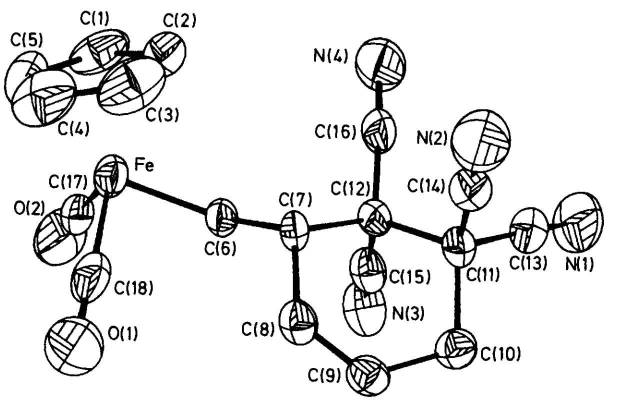


Figure 1. ORTEP drawing of the Fe adduct (**2b**). Pertinent bond distances: Fe–C(6) 2.060(5), C(6)–C(7), 1.535(7), C(7)–C(8) 1.501(7), C(7)–C(12) 1.572(7), C(8)–C(9) 1.311(7), C(9)–C(10) 1.497(7), C(10)–C(11) 1.552(7), C(11)–C(12) 1.575(7).

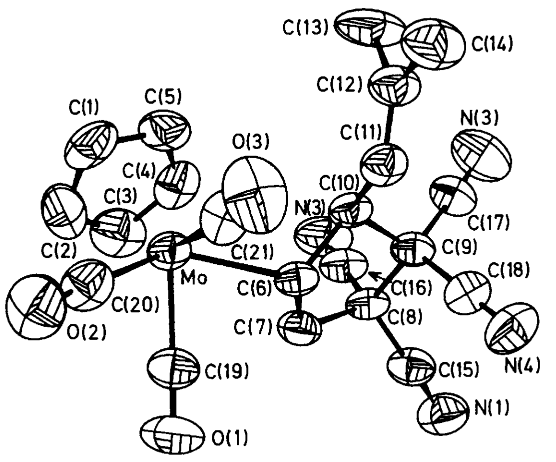


Figure 2. ORTEP drawing of the Mo adduct (**3e**). Pertinent bond distances: Mo–C(6) 2.335(5), C(6)–(7) 1.521(6), C(6)–C(10) 1.542(6), C(7)–C(8) 1.584(6), C(8)–C(9) 1.574(6), C(9)–C(10) 1.573(6), C(10)–C(11) 1.492(8), C(11)–C(12) 1.312(6), C(12)–C(13) 1.512(8), C(12)–C(14) 1510(7).

penta-2,4-dien-1-yl ligand of the iron complex (**1b**) underwent 1,4-addition with TCNE to form a cyclohexene ring, whereas the 5-methylhexa-2,4-dien-1-yl ligand of the molybdenum complex (**1e**) underwent 1,3-addition with TCNE to form a cyclopentane ring. In the latter complex, the vinyl group is *trans* to the Mo–C(6) bond, with the $CpMo(CO)_3$ subunit migrating to the β-carbon of the dienyl ligand, suggesting an ionic cycloaddition mechanism, as for the [3 + 2]cycloaddition of iron–σ-allyl complexes with reactive alkenes.[6,7]

Treatment of (**1b**) with reactive alkynes hexafluorobut-2-yne and dimethyl acetylenedicarboxylate in dichloromethane at 23 °C similarly led to a 1 : 1 adduct (**4b**) in moderate yields.§ The compounds were isolated as pure red oils after purification on an alumina column. Spectroscopic data indicate that the adduct results from insertion of the alkynes into the iron–σ-carbon bond of the parent compound. For the hexafluorobut-2-yne adduct (**4b**; E = CF_3), the two CF_3 groups are mutually *trans* as indicated by the ^{19}F n.m.r. spectra which show two singlet CF_3 resonances at 62.4 and 56.6 p.p.m.[7] Notably, complexes (**1a**) and (**1c**) do not undergo insertion with the alkynes. We believe that the insertion proceeds *via* an ionic mechanism analogous to the 1,3-allyl rearrangement in the reaction of the complex $CpFe(CO)_2$(σ-allyl) with SO_2.[8]

We have presented the model reactions which show the versatile reactivity of the related transition metal pentadienyls. In comparison with their main group analogues, these compounds have greater potential in organic reactions owing to their multiple functional groups.

Received, 2nd March 1988; Com. 8/00844B.

References

1 D. Seyferth, J. Pornet, and R. M. Weinstein, *Organometallics*, 1982, **1**, 1651; D. Seyferth and J. Pornet, *J. Org. Chem.*, 1980, **45**, 1721; A. Gopalan, R. Moerck, and P. Magnus, *J. Chem. Soc., Chem. Commun.*, 1979, 548.
2 H. Yasuda, T. Nishi, S. Miyanaga, and A. Nakamura, *Organometallics*, 1985, **4**, 359; A. Hosomi, M. Saito, and H. Sakurai, *Tetrahedron Lett.*, 1980, **21**, 3783.
3 S. F. Lush and R. S. Liu, *Organometallics*, 1986, **5**, 1908; G. H. Lee, S. M. Peng, T. W. Lee, and R. S. Liu, *ibid.*, 1986, **5**, 2378.
4 T. W. Lee and R. S. Liu, *J. Organomet. Chem.*, 1987, **320**, 211.
5 G. H. Lee, S. M. Peng, S. F. Lush, M. Y. Liao, and R. S. Liu, *Organometallics*, 1987, **6**, 2094.
6 W. P. Giering, S. Raghu, M. Rosenblum, A. Cutler, D. Ehntholt, and R. W. Fish, *J. Am. Chem. Soc.*, 1972, **94**, 8251.
7 J. P. Williams and A. Wojcicki, *Inorg. Chem.*, 1977, **16**, 3116.
8 W. P. Giering and M. Rosenblum, *J. Am. Chem. Soc.*, 1971, **93**, 5299.

---

§ *Spectroscopic data* for (**4b**; E = CO_2Me): i.r.(Nujol), ν(CO) 2030(s), 1980(s), 1770(s) cm^{-1}, ν(C=C) 1650(s) cm^{-1}; ^1H n.m.r. (400 MHz, C_6D_6), δ 3.40(d, 2H, *J* 6.2 Hz), 3.45(s, 3H), 3.46(s, 3H), 4.39(s, 5H), 4.87(dd, 1H, *J* 9.4, 1.2 Hz), 5.05(dd, 1H, *J* 15.6, 1.2 Hz), 5.87(m, 1H), 6.19(dd, 1H, *J* 13.3, 11.0 Hz), 6.28 (m, 1H); ^{13}C-{H} n.m.r. (100 MHz, C_6D_6), δ 28.1 (CH_3), 30.1 (CH_3'), 38.9, 86.8 (C_5H_5), 115.4, 132.3, 133.0, 137.6, 139.3 (Fe–*C*=), 153.4(Fe–C=*C*), 170.0, 177.1, 214.0.

For (**4b**; E = CF_3): i.r.(Nujol), ν(CO) 2040(s), 2000(s), ν(C=C), 1600(m) cm^{-1}; ^1H n.m.r. (400 MHz, C_6D_6), δ 2.91(m, 2H), 4.20(s, 5H), 4.90(d, 1H, *J* 10.8 Hz), 5.01 (d, 1H, *J* 16.4 Hz), 5.58(m, 1H), 6.06(dd, 1H, *J* 15.0, 10.8 Hz), 6.14(m, 1H); ^{13}C n.m.r. (100 MHz, C_6D_6), δ 36.8, 86.2 (C_5H_5), 115.9, 132.2, 133.1, 135.5, 139.9 (Fe–*C*=C, q, J_{CF} 29 Hz), 141.2 (Fe–C=*C*, q, J_{CF} 29 Hz), 129.5, 133 ($2CF_3$, q, J_{CF} 270 Hz, 213.6); ^{19}F n.m.r. (93.6 MHz, C_6D_6), δ 56.69(s), 62.4(s) p.p.m.