

Pentacarbonyl(η^2 -*cis*-cyclo-octene)chromium: Photochemical Synthesis of a Useful $\text{Cr}(\text{CO})_5$ Transfer Reagent

Friedrich-Wilhelm Grevels and Volker Skibbe

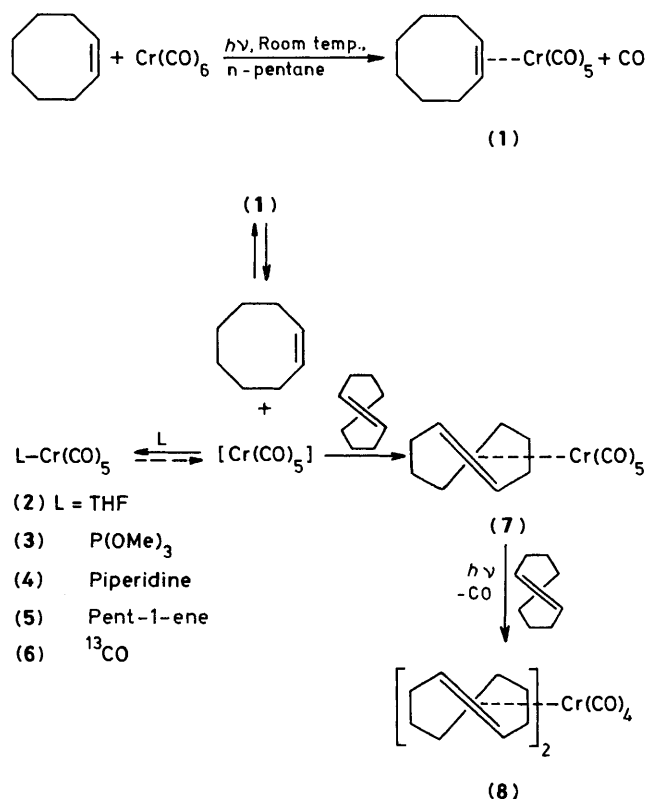
Max-Planck-Institut für Strahlenchemie, Stiftstrasse 34–36, D-4330 Mülheim a.d. Ruhr, Federal Republic of Germany

(η^2 -Olefin) $_n\text{Cr}(\text{CO})_{6-n}$ complexes result from the photoreactions of $\text{Cr}(\text{CO})_6$ with *cis*-cyclo-octene ($n = 1$) and *trans*-cyclo-octene ($n = 1, 2$); (η^2 -*cis*-cyclo-octene) $\text{Cr}(\text{CO})_5$, isolated as a yellow solid, is labile in solution and serves as a useful $\text{Cr}(\text{CO})_5$ transfer reagent to produce various $\text{LCr}(\text{CO})_5$ derivatives, including the isotopically labelled hexacarbonyl, $\text{Cr}(\text{CO})_5(^{13}\text{CO})$.

Photosubstitution of group 6a metal hexacarbonyls has been established to occur with high quantum yield¹ and has found a wide range of applications,² mainly with n -donor ligands. Olefin substituted derivatives are less well documented, although they are of particular relevance with respect to photocatalytic processes³ such as olefin isomerization.⁴ Various (η^2 -olefin) $_n\text{M}(\text{CO})_{6-n}$ complexes^{4,5} ($n = 1, 2$) have been generated photochemically from hexacarbonyl-tungsten and -molybdenum. With one exception, (tetracyanoethene)- $\text{Cr}(\text{CO})_5$,⁶ the analogous chromium complexes are not yet known. In this paper we report on the first compounds of this type with unsubstituted olefinic ligands.

Photolysis of hexacarbonylchromium and an excess of *cis*-cyclo-octene in *n*-pentane results in the formation of (η^2 -*cis*-cyclo-octene) $\text{Cr}(\text{CO})_5$ (**1**). The product crystallizes, together with residual $\text{Cr}(\text{CO})_6$, upon cooling the concentrated solution to -78°C . The $\text{Cr}(\text{CO})_6$ is removed by sublimation at $0^\circ\text{C}/<10^{-3}$ Torr and the remaining product is recrystallized from *n*-pentane doped with 5% *cis*-cyclo-octene. A typical run [20 mmol $\text{Cr}(\text{CO})_6$, 20 ml *cis*-cyclo-octene, 400 ml *n*-pentane; Solidex glass immersion well apparatus, Philips HPK 125 W mercury lamp, *ca.* 20 h irradiation at room temp.] affords *ca.* 4.5 g of complex (**1**) as a yellow crystalline substance [m.p. 62°C , decomp.; $\tilde{\nu}(\text{CO})$ 2070.5m, 1953.5s, 1948sh. cm^{-1} , in *n*-hexane–5% *cis*-cyclo-octene].[†]

The solid material is stable enough to be handled at room temperature. However, in solution above -40°C the complex



Scheme 1

[†] A satisfactory elemental analysis was obtained.

Table 1. ^{13}C N.m.r. data^a of the complexes (1), (7), and (8).

	δ	$-\text{CH}=\Delta\delta$		$-\text{CH}_2-\delta$		$\text{CO(ax.)}\delta$	$\text{CO(eq.)}\delta$	Temp. °C
(1)	90.9	39.4	30.9	29.3	25.6	224.7	216.5	-60
(7)	87.9	46.0	40.3	36.5	28.3	224.6	217.1	0
(8)	71.7	62.2	41.0	37.1	29.3	—	221.7	0

^a In $(^2\text{H}_6)$ toluene, using a Bruker WH 270 (67.89 MHz).

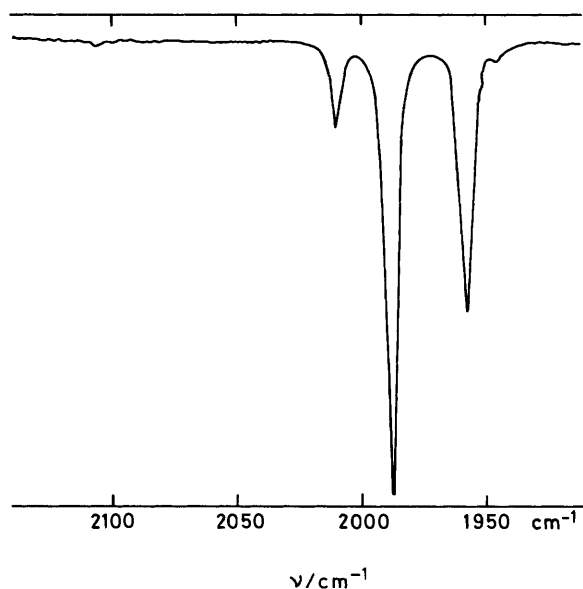


Figure 1. Infrared CO stretching vibrational pattern of $\text{Cr}(\text{CO})_5(^{13}\text{CO})$ (6) [$\bar{\nu}(\text{CO})$ 2106.5, 2100, 1987.5, and 1957 cm^{-1} , in n-hexane].

gradually decomposes with formation of $\text{Cr}(\text{CO})_6$, unless an excess of *cis*-cyclo-octene is present. Rapid, and complete, conversion into $\text{Cr}(\text{CO})_6$ occurs upon treatment of an alkane solution of (1) with carbon monoxide. This reaction is significantly retarded if carried out in the presence of an excess of *cis*-cyclo-octene, thus pointing towards a dissociative mechanism involving the facile, reversible loss of the olefinic ligand (Scheme 1).

These observations tempted us to examine the possible displacement of *cis*-cyclo-octene by various other ligands (Scheme 1). As monitored by i.r. spectroscopy, $(\text{THF})\text{Cr}(\text{CO})_5$ (2) is formed upon dissolving (1) in tetrahydrofuran (THF) [$\bar{\nu}(\text{CO})$ 2073vw, 1937.5s, 1895.5m cm^{-1}]. The spectra recorded in THF-*cis*-cyclo-octene mixtures indicate that the two complexes, (1) and (2), coexist in comparable concentrations. The reactions of (1) with strong n-donor ligands such as trimethylphosphite and piperidine result in quantitative formation of (3) and (4).⁷ (η^2 -Pent-1-ene) $\text{Cr}(\text{CO})_5$ (5) is generated by dissolving (1) in pent-1-ene [$\bar{\nu}(\text{CO})$ 2074m, 1957.5s, 1951sh. cm^{-1}]; as expected, the CO stretching bands of the α -olefin complex are shifted to higher wavenumbers by 3–4 cm^{-1} compared with (1). These experiments indicate that (1) represents a useful alternative to the

THF complex (2) as a source of the $\text{Cr}(\text{CO})_5$ unit. ‡ Moreover, (1) has the particular advantage that it is readily accessible as a pure compound which, by contrast to *in situ* generated $(\text{THF})\text{Cr}(\text{CO})_5$,⁷ is not contaminated with residual $\text{Cr}(\text{CO})_6$.

An intriguing example of this is the preparation of $\text{Cr}(\text{CO})_5(^{13}\text{CO})$. ^{13}CO -Labelling is a powerful tool in spectroscopic studies on carbonyl-metal complexes and fragments.⁸ In general, photo-induced exchange of CO ligands for ^{13}CO results in a scrambled mixture of molecules with statistical distribution of the label. By contrast, the reaction of (1) with ^{13}CO in n-hexane-*cis*-cyclo-octene (9:1) yields the mono-labelled $\text{Cr}(\text{CO})_5(^{13}\text{CO})$ (6) with 6% $\text{Cr}(\text{CO})_4(^{13}\text{CO})_2$ and 3% $\text{Cr}(\text{CO})_6$. This result of the mass spectrometric analysis corresponds to the isotopic purity of the ^{13}CO gas and to the natural abundance of ^{13}CO in complex (1). The i.r. pattern in the metal carbonyl region (Figure 1) is in agreement with those bands in the spectrum of a $\text{Cr}(\text{CO})_{6-n}(^{13}\text{CO})_n$ mixture^{8a} which were assigned to the species with $n = 1$.

trans-Cyclo-octene forms a pentacarbonylchromium complex (7) which, in contrast to (1), is stable in solution. Compound (7) [pale yellow crystals, m.p. 59 °C; $\bar{\nu}(\text{CO})$ 2070.5m, 1960s, 1954.5s cm^{-1} , in n-hexane]† is readily accessible from (1) in nearly quantitative yield by simple olefin exchange at room temperature. The enhanced stability of the metal-olefin bond, probably owing to a substantial relief from ring strain upon complexation,⁹ is reflected in a higher ^{13}C n.m.r. co-ordination shift ($\Delta\delta$) of the olefinic carbon atoms (Table 1) of (7), compared with (1). The photoreaction of $\text{Cr}(\text{CO})_6$ and *trans*-cyclo-octene provides an alternative, direct route to (7). However, unlike (*cis*-cyclo-octene) $\text{Cr}(\text{CO})_5$, (7) undergoes further photo-substitution of CO for a second olefinic ligand (Scheme 1). Extended photolysis of hexacarbonylchromium in the presence of an excess of *trans*-cyclo-octene finally results in nearly quantitative formation of (η^2 -*trans*-cyclo-octene) $_2\text{Cr}(\text{CO})_4$ (8) (pale yellow crystals, m.p. > 200 °C, decomp.). † The ^{13}C n.m.r. and i.r. spectroscopic data indicate the equivalence of the four CO ligands with a possible, albeit small deviation from coplanarity: we observe only one ^{13}CO n.m.r. signal and one strong i.r. CO stretching band ($\bar{\nu}$ 1937 cm^{-1} , in n-hexane) together with two very weak absorptions (2024, 1973 cm^{-1}) which are less intense than the ^{13}CO satellite band (1908 cm^{-1}). Hence it follows that, by analogy with *trans*-(η^2 -methyl acrylate) $\text{W}(\text{CO})_4$,^{5b} the two olefinic ligands of (8) occupy *trans*-positions in the octahedral complex, most probably with a staggered orientation of the double bonds.^{5b,10} In going from (7) to (8) the olefinic carbon atoms experience a drastically

‡ A substantially improved yield of, e.g., a sulphur ylide $\text{Cr}(\text{CO})_5$ complex was obtained with (1) in alkane solution, instead of (2) in THF, as the $\text{Cr}(\text{CO})_5$ source; L. Weber, Universität Essen, personal communication.

increased high field co-ordination shift (Table 1) in agreement with a substantial strengthening of the metal-olefin bond.

Received, 23rd January 1984; Com. 086

References

- 1 W. Strohmeier and D. von Hobe, *Chem. Ber.*, 1961, **94**, 761; J. Nasielski and A. Colas, *Inorg. Chem.*, 1978, **17**, 237.
 - 2 W. Strohmeier, *Angew. Chem.*, 1964, **76**, 873; *Angew. Chem., Int. Ed. Engl.*, 1964, **3**, 730; E. Koerner von Gustorf and F.-W. Grevels, *Top. Curr. Chem.*, 1969, **13**, 366; G. L. Geoffroy and M. S. Wrighton, 'Organometallic Photochemistry,' Academic Press, New York, 1979.
 - 3 L. Moggi, A. Juris, D. Sandrini, and M. F. Manfrin, *Rev. Chem. Intermed.*, 1981, **4**, 171; M. S. Wrighton, J. L. Graff, C. L. Reichel, and R. D. Sauner, *Ann. N.Y. Acad. Sci.*, 1980, **333**, 188.
 - 4 M. Wrighton, G. S. Hammond, and H. B. Gray, *J. Organomet. Chem.*, 1974, **70**, 283.
 - 5 (a) I. W. Stolz, G. R. Dobson, and R. K. Sheline, *Inorg. Chem.*, 1963, **2**, 1264; (b) F.-W. Grevels, M. Lindemann, R. Benn, R. Goddard, and C. Krüger, *Z. Naturforsch., Teil B.*, 1980, **35**, 1298.
 - 6 M. Herberhold, *Angew. Chem.*, 1968, **80**, 314; *Angew. Chem., Int. Ed. Engl.*, 1968, **7**, 305.
 - 7 W. Strohmeier and F.-J. Müller, *Chem. Ber.*, 1969, **102**, 3608; R. Mathieu, M. Lenzi, and R. Poilblanc, *Inorg. Chem.*, 1970, **9**, 2030; R. J. Dennenberg and D. J. Darensbourg, *ibid.*, 1972, **11**, 72.
 - 8 (a) R. N. Perutz and J. J. Turner, *Inorg. Chem.*, 1975, **14**, 262; (b) P. S. Braterman, 'Metal Carbonyl Spectra,' Academic Press, London, 1975.
 - 9 M. von Büren and H.-J. Hansen, *Helv. Chim. Acta*, 1977, **60**, 2717; M. von Büren, M. Cosandey, and H.-J. Hansen, *ibid.*, 1980, **63**, 892.
 - 10 C. Bachmann, J. Demuyunck, and A. Veillard, *J. Am. Chem. Soc.*, 1978, **100**, 2366.
-