troscopically and chromatographically identical with a sample of **20** produced in the same way from bilobalide-derived **19**. Synthetic diol **20** was converted to bilobalide 6-acetate (**22**) by a two-step process: (1) reaction with methyl oxalyl chloride (1.3 equiv) and diisopropylethylamine (2 equiv) in acetonitrile at 0 °C for 2 h to form **21** in 100% yield and (2) reaction in dilute toluene solution at reflux with a low concentration of tri-*n*-butyltin hydride (3 equiv of a 0.05 M solution in toluene containing 0.05 equiv of azobisisobutyronitrile added by syringe drive over 4 h) to give the (±)-bilobalide acetate **22**, mp 270–274 °C (55%), along with recovered diol **20** (30%).[14] Synthetic (±)-**22** was identical with an authentic sample of bilobalide acetate[1] by 500-MHz ^1H NMR, infrared, mass spectral, and TLC comparison. Hydrolysis of synthetic (±)-**22** with 3 N hydrochloric acid at reflux for 36 h afforded (±)-bilobalide **1** (70% yield), spectroscopically and chromatographically identical with an authentic sample.[15] The synthesis of (±)-bilobalide described above solves one of the classical problems of organic synthesis by the use of novel chemistry and highly selective reactions. The one-step synthesis of **2** is both unprecedented and practical. In addition the conversions **7** → **9**, **9** → **12**, **12** → **13**, **18** → **19**, and **19** → **1** are noteworthy. The unusual *tert*-butylcarbinol unit of **1** greatly complicates the task of synthesis because the conventional methods of synthesis are inapplicable.[16]

Supplementary Material Available: Spectral and analytical data for **1–3**, **5–7**, **9a**,**9b**, **10–16**, and **17–22** (3 pages). Ordering information is given on any current masthead page.

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[14] See: Dolan, S. C.; MacMillan, J. *J. Chem. Soc., Chem. Commun.* **1985**, 1588–1589. It is essential that the tin hydride be added slowly, otherwise the production of diol **20** increases relative to **22**.

[15] We are grateful to Dr. Pierre Braquet, Institute Henri Beaufour, Le Plessis Robinson, France, for a generous sample of naturally derived bilobalide.

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Photoreactions of Group 6 Metal Carbonyls with Ethene: Syntheses of *trans*-(η^2-Ethene)$_2$M(CO)$_4$ (M = Cr, Mo, W)

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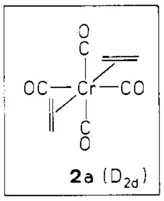
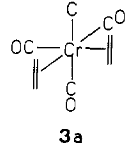
Photolysis of $Cr(CO)_6$ in ethene-doped liquid xenon at −78 °C has been reported[1] to yield (η^2-ethene)$Cr(CO)_5$ (**1a**), *trans*-(η^2-ethene)$_2Cr(CO)_4$ (**2a**), and *cis*-(η^2-ethene)$_2Cr(CO)_4$ (**3a**). All three compounds were said to be thermally unstable under these experimental conditions, their stability decreasing in the order **1a** > **2a** > **3a**. More recently[2] **1a** was photochemically generated from $Cr(CO)_6$ and ethene in the gas phase. Subsequent pulsed-laser photolysis produced a transient species, detected by means of time-resolved IR spectroscopy, which decayed on the ms time scale and was assigned as *cis*-(η^2-ethene)$_2Cr(CO)_4$ (**3a**). The lability and cis structure of **3a** was set in contrast with the stability and trans configuration of the known (η^2-olefin)$_2M(CO)_4$ complexes of molybdenum and tungsten.[3,4]

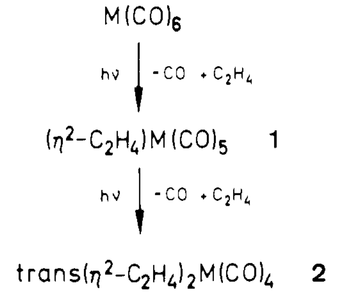


2a (D_{2d})



3a

Scheme I[a]



[a] M = Cr (**1a**, **2a**), Mo (**1b**, **2b**), W (**1c**, **2c**).

Table I. Spectroscopic and Analytical Data of **2a–c**

	2a	**2b**	**2c**
$\bar{\nu}$(CO),[a] cm^{-1}	≃1986 (vw) 1952.5 (vst)	1997.5 (vw) 1965 (vst)	1991 (vw) 1965 (vst)
δ (^1H)[b]	2.27	2.33	2.11
δ ($^{13}C\{^1H\}$)[b] C_2H_4	48.25	41.89	31.26
CO	220.44	208.74	198.08
C found (calcd)	43.42 (43.65)	36.45 (36.38)	27.86 (27.30)
H	3.62 (3.66)	3.16 (3.05)	2.09 (2.29)
metal	23.72 (23.62)	36.21 (36.33)	52.32 (52.23)

[a] In *n*-hexane. [b] In toluene-d_8.

This conflicts with our experience with olefin-substituted group 6 metal carbonyls[3,5–7] and led us to suspect that the apparent disconformity should not be associated with the particular metal but rather originates from differences in the reaction conditions, i.e., gas-phase photochemistry in the chromium case[2] vs photoreactions of the molybdenum and tungsten compounds in solution.[3,4,6,7] Recent experiments allow us to expand on this point and prompt us to report on the photoreaction of $Cr(CO)_6$ with ethene in alkane solution, which provides convenient preparative access to the *stable trans*-(η^2-ethene)$_2Cr(CO)_4$ (**2a**).

Irradiation of $Cr(CO)_6$ (10 mM) in ethene-saturated pentane solution (solidex immersion well apparatus, λ ≥ 280 nm; Philips HPK 125-W mercury lamp) leads to sequential photosubstitution of CO for ethene; Scheme I, M = Cr. As monitored by infrared spectroscopy,[8] initially formed **1a** [$\bar{\nu}$(CO) = 2078 (w), 1967 (st), 1961.5 (vst) cm^{-1}][9] is largely converted into *trans*-(η^2-ethene)$_2Cr(CO)_4$ (**2a**)[9] upon extended irradiation. The first step is most conveniently performed at −20 °C, whereas the second step requires cooling to −50 °C. After filtration of the concentrated solution over silica gel and recrystallization from pentane, pure **2a** is obtained as pale yellow crystals, mp 67–68 °C, 30% yield.

Relevant spectroscopic and analytical data on **2a** are summarized in Table I. The observation of only one strong CO stretching vibrational band in the IR spectrum immediately rules out a *cis*-(η^2-ethene)$_2Cr(CO)_4$ structure [**3a**; four IR active ν(CO) vibrations] in favor of the *trans*-(η^2-ethene)$_2Cr(CO)_4$ geometry, most probably with orthogonal orientation of the two ethene ligands [D_{2d} symmetry; ν(CO): a_1 (IR inactive), b_2 (formally IR active, but extremely weak), e (IR active, very strong)]. This has been confirmed by the X-ray structure analysis of **2a**.[10] The ^1H and $^{13}C\{^1H\}$ NMR spectra (Table I) exhibit only one and two signals, respectively, in accordance with structure **2a**.

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(9) The IR data of **1a** and **2a** are in good agreement with those obtained in liquid xenon.[1]

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trans-(η^2-Ethene)$_2$Cr(CO)$_4$ (**2a**) is thermally stable not only in the solid state but also in the gas phase,[11] in liquid xenon,[12] and in alkane solution. By contrast, (η^2-ethene)Cr(CO)$_5$ (**1a**) is only moderately stable. Monitoring a **1a**/**2a** mixture in ethene-saturated alkane solution at ambient temperature by infrared spectroscopy we observe that **1a** decomposes gradually with formation of Cr(CO)$_6$, whereas **2a** survives for an extended period of time. Under CO atmosphere **1a** has vanished within a few minutes, but **2a** is still present after several hours, as long as oxygen is strictly excluded.

The photoreactions of Mo(CO)$_6$ and W(CO)$_6$ take essentially the same route as illustrated for Cr(CO)$_6$; Scheme I, M = Mo, W. The only difference is that the formation of **2c** via **1c** [M = W; $\bar{\nu}$(CO) = 2085.5 (w), 1974 (st), 1955.5 (vst) cm^{-1}] occurs at ambient temperature, and the synthesis of **2b** via **1b** [M = Mo; $\bar{\nu}$(CO) = 2086 (w), 1976 (st), $\simeq$1960 (vst) cm^{-1}] is most conveniently performed at −20 °C. The photochemical generation of these compounds has been reported previously together with their infrared data,[4] but they were considered to be too unstable for isolation. However, we have obtained both of the two *trans*-(η^2-ethene)$_2$M(CO)$_4$ complexes as colorless crystals: **2b**, mp 70–73 °C, 48% yield; **2c**, mp 130–135 °C, 52% yield. The spectroscopic data (Table I) closely resemble those of **2a**, and consequently the same structure can be assigned.

In all our experiments we see no evidence for the formation of any of the *cis*-(η^2-ethene)$_2$M(CO)$_4$ complexes **3**, but we have to consider the possibility that such a species could be involved as a short-lived intermediate.[8] In fact, ab initio calculations[13] on L-Mo(CO)$_5$ and low-temperature matrix experiments with (η^2-olefin)W(CO)$_5$ in alkane glass[14] or solid argon[7] indicate initial photodissociation of cis CO. Nevertheless, we find it remarkable that in the gas-phase experiments[2] with (η^2-ethene)Cr(CO)$_5$ and ethene the cis product **3a** is the only observable (η^2-ethene)$_2$Cr(CO)$_4$ species, and no trace of the stable trans isomer **2a** was observed. A plausible explanation[15] is that the formation of the latter involves **3a** → **2a** photoisomerization.[16] At ambient temperature in the gas phase (or in alkane solution) this photoisomerization may be outstripped by the thermal decay of **3a**. Cooling will provide sufficient stabilization of **3a**, such that its photochemical rearrangement to **2a** becomes feasible, as it happens in liquid xenon[1] or in alkane solution at −50 °C. In going from Cr to Mo and W the stability of type **3** complexes is expected to increase, and, consequently, cooling would become less essential in order to render the **3** → **2** photorearrangement feasible.

In a control experiment we used (η^4-dimethylbutadiene)Cr(CO)$_4$ (**4**)[17] as a source of the *cis*-Cr(CO)$_4$ unit.[18] Upon treatment with ethene at ambient temperature in the dark **4** disappears gradually with formation of (η^2-ethene)Cr(CO)$_5$ (**1a**) and Cr(CO)$_6$ as the only soluble products. Most probably these compounds originate from decomposition of labile *cis*-(η^2-ethene)$_2$Cr(CO)$_4$ (**3a**). However, no trace of *trans*-(η^2-ethene)$_2$Cr(CO)$_4$ (**2a**) could be detected, thus providing indirect evidence for the involvement of a second photochemical step, $\mathbf{3a} \xrightarrow{h\nu} \mathbf{2a}$, in the synthesis of the latter.

In conclusion we note that the coordination of two ethene ligands to the Cr(CO)$_4$ moiety nicely parallels the molybdenum and tungsten analogues: all three metals form stable *trans*-(η^2-ethene)$_2$M(CO)$_4$ complexes **2**. This and the distinctly lower stability of (η^2-ethene)M(CO)$_5$ **1** and *cis*-(η^2-ethene)$_2$M(CO)$_4$ **3** species is easily understood in terms of optimum metal → π^* (olefin) back donation.[6,7,19-21] Two olefins in trans orthogonal orientation do not compete for metal (d$_\pi$) electron density, owing to their single-faced π-acceptor character. By contrast a CO ligand (with its *two* orthogonal π-acceptor orbitals) situated trans to an olefin will strongly rival, thus weakening the metal–olefin bond.

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(11) In the gas-phase IR spectrum of **2a** the intensity of the strong ν(CO) band (1967 cm^{-1}) remains constant over several hours.

(12) The apparent lability of **2a** in liquid xenon[1] was disproven by using a pure sample of the complex: M. Poliakoff, private communication.

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(15) We are grateful to the referees for drawing our attention to this point.

(16) The reverse process, **3a** → **2a** photoisomerization, was observed under low-temperature matrix isolation conditions: Klotzbücher, W. E., private communication.

(17) Prepared by analogy with other (η^4-1,3-diene)Cr(CO)$_4$ compounds: Fischler, I.; Budzwait, M.; Koerner von Gustorf, E. A. *J. Organomet. Chem.* **1976**, *105*, 325–330. **4**: $\bar{\nu}$(CO) = 2037.5, 1980, 1937.5, 1934 cm^{-1}; in *n*-hexane.

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Novel Catalytic Chemistry of Iridium Polyhydride Complexes

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Polyhydride complexes of transition metals ([MH$_x$L$_y$], where L is a ligand such as a tertiary phosphine), constitute a distinctive class of compounds which have been widely studied in other contexts[1] but whose catalytic chemistry has not thus far been extensively explored. Earlier studies[2,3] have demonstrated the effectiveness of polyhydride complexes, e.g., [RuH$_2$(PPh$_3$)$_2$(PPh$_2$C$_6$H$_4$)]$^-$, [RuH$_3$(PPh$_3$)$_3$]$^-$, [RuH$_5$(PPh$_3$)$_2$]$^-$, and [RuH$_4$(PPh$_3$)$_3$], as catalysts or catalyst precursors for the hydrogenation of a variety of substrates including ketones, esters, and arenes which are not readily hydrogenated by most other homogeneous catalysts. Distinctive features of these systems appear to include the ability of such polyhydride complexes to serve as highly loaded "hydrogen reservoirs" and the accessibility of vacant coordination sites through the facile reductive elimination or transfer of coordinated hydrogen.

Extending these studies we now have uncovered significantly different reactivity patterns for the iridium polyhydride complex [IrH$_5$P$_2$] (P = P-*i*-Pr$_3$)[4] and derivatives thereof, some features of which are unprecedented. We report here preliminary results of these studies.

[IrH$_5$P$_2$] reacts with the activated ester CF$_3$COOR (R = CH$_2$CF$_3$) in cyclo-C$_6$D$_{12}$[5] at 60 °C to yield [IrH$_2$P$_2$(OR)][6] in

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(1) For leading references, see: (a) Moore, D. S.; Robinson, S. D. *Chem. Soc. Rev.* **1983**, 415–452. (b) Caulton, K. G. *Ann. N. Y. Acad. Sci.* **1983**, *415*, 27–36.

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(5) Deuteriated aromatic solvents could not be used in these studies because of facile isotopic exchange with [IrH$_5$P$_2$].

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