ward highly purified carbon dioxide are illustrative:

Addition of hexane to THF solutions of Rh(4-MeC_6H_4)(bdpp) that had been pressured to 40–45 bar of rigorously dried and deoxygenated CO_2 afforded a yellow material, the IR spectrum of which closely resembled that of 1 except for the absence of the 1255 cm^{-1} band. Unlike 1, however, this substance turned out to be readily soluble in toluene. The ^{31}P NMR spectrum of a freshly prepared C_7H_8 solution recorded at 273 K (Figure 2) consisted of two overlapping spin systems characterized by the following: (1) $\delta(PPh_2)$ 15.9, $\delta(PPh)$ 0.2 ($^1J(Rh–PPh_2)$ = 157 Hz, $^1J(Rh–PPh)$ = 107 Hz, $^2J(PP)$ = 46 Hz (starting material));[12] (2) $\delta(PPh_2)$ 7.9, $\delta(PPh)$ 21.0 ($^1J(Rh–PPh_2)$ = 134 Hz, $^1J(Rh–PPh)$ = 160 Hz, $^2J(PP)$ = 55 Hz (marked by an asterisk in Figure 2)).

Spectrum 2 was observed to gradually decrease in intensity in favor of the resonance pattern of the starting compound, the spectral changes being accompanied by CO_2 evolution from the solution. We therefore assign the labeled signals of Figure 2 to a reversible CO_2 adduct Rh(4-MeC_6H_4)(bdpp)·CO_2 containing a loosely bound carbon dioxide ligand. Due to the ease with which the gas was released from this compound either in solution or in the solid state, attempts at purification and further characterization were unsuccessful. Significantly however, exposure of solutions of freshly prepared samples to the air induced the deposition of a yellow precipitate which, upon redissolution in pyridine, was easily identified as the peroxocarbonate 1 via ^{31}P NMR.

Acknowledgment. We gratefully acknowledge a generous gift of $RhCl_3 \cdot xH_2O$ by DEGUSSA, Hanau. Thanks are also expressed to the staff of the X-ray laboratory of this institute for collecting diffraction data.

Registry No. 1, 89936-94-7; $Ir(CH_2SiMe_3)(CO)(PPh_3)_2$, 82180-73-2; $Ir(4\text{-}MeC_6H_4)(CO)(PPh_3)_2$, 59537-96-1; $Rh(CH_2SiMe_3)(CO)(PPh_3)_2$, 82180-77-6; $Rh(CH_2CMe_3)(CO)(PPh_3)_2$, 82180-78-7; $Rh(4\text{-}MeC_6H_4)(CO)(PPh_3)_2$, 82190-11-2; $Ir(CH_2SiMe_3)$(bdpp), 88492-99-3; Rh(4-MeC_6H_4)(bdpp), 84975-91-7; CO_2, 124-38-9.

Supplementary Material Available: A table of positional and thermal parameters and their estimated standard deviations and a listing of observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page.

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[12] In ref 4a, the chemical shifts $\delta(PPh_2)$ and $\delta(PPh)$ of Rh(4-MeC_6H_4)(bdpp) have mistakenly been given as 19.3 and 3.3 ppm. Correct values are (at ca. 308 K) 16.3 and 0.3 ppm, respectively.

η^3-Allyl Complexes of Molybdenum: The Preparation and Structure of $[Mo(\eta^3\text{-}C_3H_5)_2(\eta^5\text{-}C_5H_5)]$

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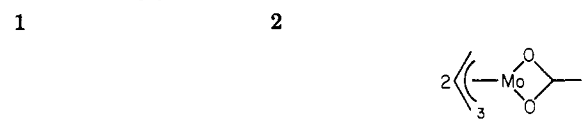
Summary: Tetra(η^3-allyl)molybdenum reacts with hydrogen chloride to give the tris(η^3-allyl)molybdenum chloride dimer. Further reaction with donor ligands causes monomerization while treatment with sodium cyclopentadienide leads to the formation of the paramagnetic complex $[Mo(\eta^3\text{-}C_3H_5)_2(\eta^5\text{-}C_5H_5)]$ whose crystal structure has been determined by X-ray methods.

Although $[Mo(\eta^3\text{-}C_3H_5)_4]$ (1) has been known for 20 years,[1] supposed difficulties in its preparation have deterred a systematic investigation of its chemistry and it has even been suggested that it is relatively unreactive. We describe here an improved preparation and some representative reactions.

Addition of solid $MoCl_4 \cdot 2THF$ to a 20% excess of allylmagnesium chloride at room temperature in diethyl ether leads to the formation of 1 (ca. 40% yield)[2] as a sublimable, yellow solid without significant contamination from the green dimer $[Mo_2(\eta^3\text{-}C_3H_5)_4]$.

1 reacts quantitatively with HCl(g) at -70 °C in pentane and with iodine at -40 °C in diethyl ether with substitution of an allyl group by a halide to give $[MoCl(\eta^3\text{-}C_3H_5)_3]_2$ (2) as a pentane-insoluble pink solid stable below -30 °C and $[MoI(\eta^3\text{-}C_3H_5)_3]_2$ as a red-brown solid stable below -20 °C; both presumably as dimers. Treatment of the chloride with silver acetate leads to the formation of the pentane-soluble acetate 3 as a yellow solid that slowly decomposes at room temperature and melts with decomposition at 57 °C. The NMR spectra of 3 indicate the magnetic inequivalence of the three allyl groups.[3]



1

2

3

The chloride 2 and iodide have long been implied as the active species in the molybdenum-catalyzed polymerization of butadiene to give a polymer consisting almost exclusively of poly(1,2-butadiene),[4] and we have confirmed that they are indeed active at room temperature: 2 will even cause slow polymerization at -30 °C to give a polymer consisting of up to ca. 90% of poly(1,2-butadiene).

The chloride bridges in 2 can be cleaved by O, N, and P donor ligands, and the complexes $[MoCl(\eta^3\text{-}C_3H_5)_3L]$ (L = py, MeCN and PMe_3) have been isolated. Here again the NMR spectra indicate an asymmetric arrangement of the allyl groups. 2 can also be taken into solution by reaction with the Lewis acid $AlCl_3$ in toluene to give a violet solution from which it can be precipitated in crystalline form by addition of diethyl ether.

Treatment of 2 with sodium or thallium cyclopentadienide results in the formation of the orange, paramagnetic (1.44 μ_B) complex $[Mo(\eta^3\text{-}C_3H_5)_2(\eta^5\text{-}C_5H_5)]$ (4). The monomeric nature of 4 in benzene solution is confirmed by a molecular weight determination (found 241

$$[MoCl(\eta^3\text{-}C_3H_5)_3]_2 + 2NaC_5H_5 \xrightarrow[-2C_3H_5\cdot]{-2NaCl} 2[Mo(\eta^3\text{-}C_3H_5)_2(\eta^5\text{-}C_5H_5)]$$

2

4

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[1] Oberkirch, W. Dissertation, Techn. Hochschule Aachen, 1963. Wilke, G.; Bogdanovič, B.; Hardt, P.; Heimbach, P.; Keim, W.; Kröner, M.; Oberkirch, W.; Tanaka, K.; Steinrücke, E.; Walter, D.; Zimmermann, H. *Angew. Chem.* **1966**, *78*, 157. Cotton, F. A.; Pipal, J. R. *J. Am. Chem. Soc.* **1971**, *93*, 5441. Candlin, J. P.; Thomas, H. *Adv. Chem. Ser.* **1974**, *No. 132*, 212.

[2] Satisfactory analytical data have been obtained for all complexes reported here. The MS of 3 and 4 showed the parent ion M^+.

[3] ^1H NMR (400 MHz, –80 °C, CD_2Cl_2): δ 4.98, 4.56, 4.53 (m, meso-H); 3.62, 1.67, 0.90 (d, anti-H); 3.19, 1.19, 0.29 (d, anti-H); 3.56, 3.29, 3.03 (d, syn-H); 3.56, 3.04, 1.33 (d, syn-H). We thank R. Benn and A. Rufinska for the interpretation of this spectrum. All details of this and those of the other compounds reported here will be discussed in an extensive publication.

[4] Stroganov, V. S.; Novikova, E. S.; Frolov, V. M. *Kinet. Catal. (Engl. Transl.)* **1982**, *23*, 845. Novikova, E. S.; Stroganov, V. S.; Frolov, V. M. *Ibid.* 1981, *22*, 1178 and references cited therein.

0276-7333/84/2303-0936$01.50/0

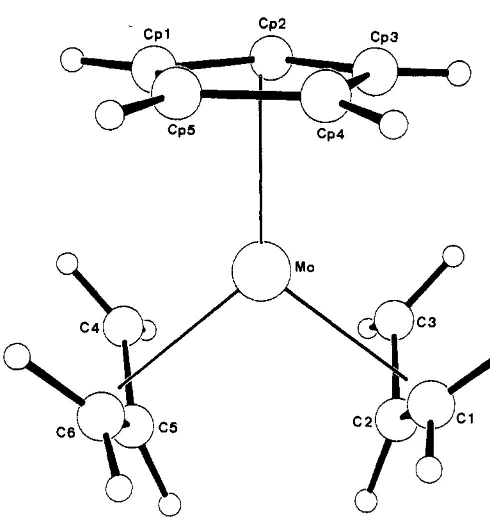

Figure 1. Molecular structure of [Mo(η^3-C_3H_5)$_2$(η^5-C_5H_5)] (4) showing the atom numbering scheme.

Table I. Selected Bond Lengths (Å) and Bond Angles (deg) for [Mo(η^3-C_3H_5)$_2$(η^5-C_5H_5)] (4)[a]

Bond Lengths			
Mo-C1	2.250 (3)	C1-C2	1.407 (4)
Mo-C2	2.248 (2)	C2-C3	1.407 (4)
Mo-C3	2.250 (3)	C4-C5	1.396 (4)
Mo-C4	2.262 (3)	C5-C6	1.414 (4)
Mo-C5	2.237 (2)	Mo-D1[b]	1.991
Mo-C6	2.252 (3)	Mo-D2[b]	1.993
Mo-C_5H_5(av)	2.345 (7)	Mo-D(Cp)[c]	2.025

Bond Angles			
C1-C2-C3	119.6 (2)	C2-Mo-C1	36.5 (1)
C6-C5-C4	119.5 (2)	C5-Mo-C2	79.8 (1)
C4-Mo-C6	65.0 (1)	C6-Mo-C1	91.6 (1)
C4-Mo-C5	36.1 (1)	C4-Mo-C3	88.6 (1)
C3-Mo-C1	65.4 (1)	D1-Mo-D2[b]	101.5
C3-Mo-C2	36.5 (1)	D1-Mo-D(Cp)[b,c]	128.4
C5-Mo-C6	36.7 (1)	D2-Mo-D(Cp)[b,c]	130.1

[a] Esd in parentheses. [b] D1 and D2 are the midpoints from the allyl groups C1-C2-C3 and C4-C5-C6, respectively. [c] D(Cp) is the midpoint from the cyclopentadienyl ring.

(cryoscopic); calcd for $C_{11}H_{15}Mo$ 243.2) and in the crystal form by the X-ray structural determination described below.

4 was recrystallized from diethyl ether as orange prisms.[5] The structure is shown in Figure 1 while important bond lengths and bond angles have been brought together in Table I. The organic ligands adopt an essentially trigonal-planar arrangement around the central metal atom.

A noncrystallographic mirror plane passes through the metal atom and bisects the five-membered ring. The two η^3-allyl groups adopt an endo, cis conformation with an angle of 25.6° between the two planes that brings the meso-hydrogen atoms H2 and H5 within 2.171 Å of each other. The plane (±0.011 Å) defined by the four terminal C atoms (C1, C3, C4, and C6) lies parallel to the plane of the cyclopentadienyl ring (±0.005 Å; 1.09°), the Mo atom being situated 2.024 (8) Å away from the latter plane and 1.029 (8) Å from the former. The geometry of the two allyl groups is very similar, the metal–carbon bonds being only slightly asymmetric: the metal atom is symmetrically bonded to the allyl group C1–C2–C3 but is closer (0.01 Å, >3 sd) to atom C6 than to atom C4 of the other group. Preliminary results of a detailed investigation of the electron deformation density by X–X methods indicate an octahedral distribution of electron density about the molybdenum atom similar to that observed in the related 17-electron compound [Fe(η^2, η^2-cod) (η^5-C_5H_5)].[6]

The analogy between the chemistry of [Mo(η^3-C_3H_5)$_4$] and [MoCl(η^3-C_3H_5)$_3$]$_2$ on the one hand and that described by Green and co-workers[7] for [Mo(η^6-C_6H_5R)$_2$] and [MoCl(η^3-C_3H_5)(η^6-C_6H_5R)] on the other has not escaped us and is being explored further. In addition work is in progress which indicates that related reactions are to be expected with the chromium and tungsten allyls, and it has, for example, proved possible to synthesize the chromium analogue for 4.[8]

Acknowledgment. C.C.R. thanks the Alexander von Humboldt Stiftung for the award of a stipendium.

Registry No. 1, 12336-10-6; 2, 89922-74-7; 3, 89922-75-8; 4 (Mo), 89922-76-9; 4 (Cr), 89922-80-5; $MoCl_4$, 13320-71-3; [MoI(η^3-C_3H_5)$_3$]$_2$, 89922-77-0; [MoCl(η^3-C_3H_5)$_3$(Py)], 89922-78-1; [MoCl(η^3-C_3H_5)$_3$(MeCN)], 89922-79-2; [MoCl(η^3-C_3H_5)$_3$(PMe$_3$], 89936-25-4; allylmagnesium chloride, 2622-05-1; butadiene, 106-99-0; poly(1,2-butadiene), 9003-17-2.

Supplementary Material Available: Listings of observed and calculated structure factors, anisotropic thermal parameters, hydrogen isotropic thermal parameters, atomic coordinates, interatomic distances, and bond angles (14 pages). Ordering information is given on any current masthead page.

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(5) X-ray diffraction data for $C_{11}H_{15}Mo$, 4: crystal size (mm), 0.5 × 0.16 × 0.1; monoclinic of space group $P2_1/a$; $a = 11.241$ (3), $b = 7.4232$ (9), $c = 12.5643$ (8) Å; $\beta = 102.715$ (8)°; $Z = 4$; $V = 1022.7$ Å^3; $d_{calcd} = 1.579$ g/cm^3; μ(Mo K_α) = 11.98 cm^{-1} (no absorption correction); $f(000) = 492$; data were collected on an Enraf-Nonius CAD-4 diffractometer; radiation Mo Kα (graphite monochromated), $\lambda = 0.71069$ Å; measured reflections ([$\pm h$, $\pm k$, l], 2° $\leq \theta \leq$ 30°), 5923; redundant data set averaged to 3169 reflections ($R_{av} = 0.026$); unique observed reflections, 2493 ($I \geq 2\sigma(I)$); number of variables, 109; structure solved by heavy-atom method; all hydrogen atom positions were located and kept fixed in the final refinement stages; $R = 0.0220$, $R_w = 0.0280$; error in an observation of unit weight, 1.53; residual electron density, 0.39 e Å^{-3}.

(6) Goddard, R.; Krüger, C., to be submitted for publication.

(7) Green, M. L. H.; Silverthorn, W. E. *J. Chem. Soc., Dalton Trans.* 1973, 301. Green, M. L. H.; Mitchard, L. C.; Silverthorn, W. E. *Ibid.* 1973, 1403, 2177.

(8) Romão, C. C., unpublished work.

Insertion Reactions of Dimethylgermylene, Me_2Ge, and Their Mechanisms As Studied by CIDNP

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Summary: The insertion of germylenes into carbon–halogen bonds is shown to occur, in the case of thermally generated Me_2Ge and benzyl bromide, via a cage abstraction–recombination reaction, giving typical ^1H CIDNP effects proving the singlet state of Me_2Ge. Besides, an abstraction reaction of escaped $\cdot GeMe_2Br$ yields Me_2GeBr_2 also showing ^1H CIDNP effects, followed by an one-step insertion of Me_2Ge into Ge–Br bonds of Me_2GeBr_2, giving oligogermanes without ^1H CIDNP effects.

Germylenes Me_2Ge can behave as heavy carbene analogues. Thus, they undergo concerted addition to a number of 1,3-dienes via a thermal [2 + 4] cheletropic mechanism.[1] Besides, several insertion reactions into σ bonds