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Preliminary communication

PREPARATION OF $(\eta^5\text{-}C_5H_5)_2MH_2$ (M = Mo, W) BY METAL VAPORATION TECHNIQUES

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Summary

$(\eta^5\text{-}C_5H_5)_2MH_2$ (M = Mo, W) have been prepared by co-condensation of metal atom vapors and cyclopentadiene at −196° in yields of 30-40% and 50-60% respectively.

Co-condensation of metal vapor and substrate is one of the latest developments in organometallic synthesis [1]**. The work of Timms [2], Skell [3,4] and others [5-8] has clearly shown that highly endothermic metal atom vapors enter into reaction with a variety of substrates upon co-condensation at low temperature. Reaction products range from simple adducts, i.e., $Cr(\eta^6\text{-}C_6H_6)_2$ [1], $Ni(PF_3)_4$ [1], etc. to products which may be considered to arise from oxidative addition of substrate to the metal atom, i.e., $M + C_6H_5X \rightarrow$ "C_6H_5MX" (M = Ni, Pd) [5b].

We wish to report what we believe to be the first examples of the formation of isolable hydrido complexes by this technique***. Co-condensation of Mo and W vapors with an excess of cyclopentadiene yields $(\eta^5\text{-}C_5H_5)_2MoH_2$ and $(\eta^5\text{-}C_5H_5)_2WH_2$ respectively. Yields of these materials were typically 30-40% for Mo and 50-60% for W. An apparatus similar to that described by Timms was utilized [10]. Tungsten atoms were obtained from a resistance heated 44 mil filament of the metal. Molybdenum atoms were obtained from 15 mil Mo wire wound on a 44 mil tungsten filament. No contamination by tungsten was noted in the latter case. Vaporization rates were 1-2 mmoles per hour. Substrate to metal ratios ranged from 10 to 100. After warming the product mixture to room temperature the excess cyclopentadiene was pumped from the reactor and the volatile dihydrides were sublimed. Final purification was by crystallization

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[**] Ref. 1 provides a recent review of the technique.

[***] Skell and co-workers have postulated hydrido intermediates to explain the composition of gaseous products from hydrolyses of metal and substrate reactions, see refs. 4 and 9. No hydride products were isolated.

from petroleum ether. (Found: C, 51.87, H, 4.92. $C_{10}H_{12}Mo$ calcd.: C, 52.64; H, 5.30%. Found: C, 38.17, H, 3.79. $C_{10}H_{12}W$ calcd.: C, 37.99, H, 3.80%.) Melting points were taken on freshly sublimed samples that were sealed under nitrogen: Mo, 174° (with darkening); W, 194-196°. These melting points were identical to those of freshly sublimed samples prepared by Wilkinson's procedure [11]. Spectroscopic data are given in Table 1. Skell reported earlier that the reaction Cr + C_5H_6 yielded chromocene and hydrogen [4]. The molybdenum and tungsten dihydrides may be considered as the products of oxidative-addition of two cyclopentadiene molecules to a single metal atom. If such a mechanism is, in fact, operative for chromium, as well as for molybdenum and tungsten, then hydrogen must be lost from $(\eta^5\text{-}C_5H_5)_2CrH_2$ in a subsequent reductive-elimination step to produce chromocene. This is quite reasonable considering the smaller size of the first row element and the generally increased stability of second and third row transition metal hydrides.

TABLE 1

SPECTROSCOPIC DATA FOR DIHYDRIDES[a]

		IR[b]	NMR[c]		
		ν(M—H) (cm^{-1})	chemical shifts, τ (ppm)		coupling constants (Hz)
			C_5H_5	hydride	
$(\eta^5\text{-}C_5H_5)_2MoH_2$	this work	1847	5.56(singlet)	18.72(singlet)	d
	lit. 11	1847	5.64(triplet)[d]	18.76(singlet)	J(H—H) 0.96
$(\eta^5\text{-}C_5H_5)_2WH_2$	this work	1901	5.76(triplet)	22.25("9-lines")[e]	J(H—H) 0.7, J(^{193}W—H) 69
	lit. 11	1896	5.76(triplet)	22.28("7-lines")[e]	J(H—H) 0.7, J(^{193}W—H) 36.6[f]

[a] Data reported are for samples prepared by the metal vaporization technique. However, identical results (within experimental error) were obtained on samples prepared by us using Wilkinson's procedure [11]. [b] Spectra were obtained as Nujol mulls on a Perkin—Elmer 457 spectrophotometer calibrated with polystyrene. [c] Spectra were obtained on a Varian HA100 spectrometer. Deuterobenzene was used as solvent, TMS as standard. [d] We did not observe splitting of the ring proton or hydride resonances in samples prepared by metal vaporization techniques or in samples prepared by Wilkinson's procedure [11]. [e] This resonance should be observed as an eleven line pattern, however, the outer lines are very weak and are difficult to detect. [f] This value apparently was obtained incorrectly. Spectra obtained on samples prepared by the metal vaporization technique and by Wilkinson's procedure gave identical spectra with J(^{193}W—H) 69 Hz.

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