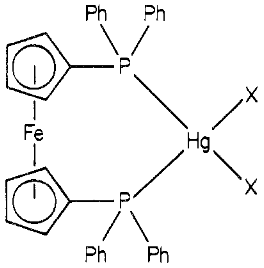
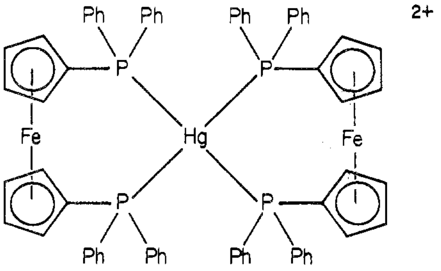
Fe–Fe interaction. If the diamagnetic nature of I is analyzed in terms of an exchange interaction (*i.e.*, $J\hat{S}_1 \cdot \hat{S}_2$) between the two $S = {}^1/_2$ Fe(III) centers, the exchange parameter J is greater than ~400 cm^{-1}. This is the case because there is no appreciable population of the triplet state ($S' = S_1 + S_2 = 1$) for I up to 300°K.

The effect of lattice contributions to the electric field gradient in I has not been included in the above analysis. It is possible that the introduction of a nearby $Fe(C_5H_5)^+$ moiety (the positive charge is most certainly *not* localized on the iron atom) is partially the cause of the large negative field gradient at the other Fe(III) in cation I. The range of quadrupole splittings for the ferricenium cation as a function of the anion is very small (0–0.08 mm/sec), but perhaps this could be attributed to the greater distances involved. However, we have just reported[11] that the quadrupole splittings observed for the two species





are essentially unchanged from that observed for ferrocene, which can be taken as evidence as to the negligible influence of a partial positive charge at a distance of ~4.0 Å or greater.

Acknowledgment. We are very grateful for support from NIH Grant HL 13652.

Registry No. Biferricenylenium bis(hexafluorophosphate), 51472-07-2.

(11) K. R. Mann, W. H. Morrison, Jr., and D. N. Hendrickson, *Inorg. Chem.*, 13, 1180 (1974).

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Transition Metal π Complexes. III. Reactions of Benzocycloheptatriene with the Group VIb Metal Carbonyls[1]

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Although transition metal π complexes of single and multiple ring systems are numerous,[2-7] analogous derivatives of the fused six-seven-membered carbocyclic benzocycloheptatriene (bcht) are unknown except for the two iron carbonyls $Fe(CO)_3(bcht)$ and $[Fe(CO)_3(bcht)]^+$.[8] This report describes results of an exploratory investigation of the reactions of bcht with the group VIb metal carbonyls and selected derivatives.

Experimental Section

Microanalyses were performed by M-H-W Laboratory, Garden City, Mich. Infrared spectra were recorded on a Model 621 Perkin-Elmer spectrometer. Proton nmr spectra were taken on a Varian Associates Model T-60 machine in chloroform-*d* with tetramethylsilane as an internal standard; carbon-13 spectra were obtained on a Jeol Model PFT-100 instrument. Mass spectra were recorded on a Varian Associates Model CH7 spectrometer. Dry nitrogen was used routinely for deaeration of solvents, maintenance of an inert atmosphere over reaction mixtures, and admission to evacuated vessels.

A mixture of 1,2- and 3,4-benzocycloheptatriene was synthesized according to a literature method beginning with 5-phenylvaleric acid.[9] The reactive intermediates $(diglyme)Mo(CO)_3$,[10] $(CH_3CN)_3Cr(CO)_3$,[11] and $(CH_3CN)_3W(CO)_3$[11] were also prepared by known procedures.

$C_{11}H_{10}Cr(CO)_3$. Equimolar amounts of chromium hexacarbonyl and bcht were allowed to react in ethylcyclohexane at 132° for 66 hr. The resulting yellow solution was cooled at −78° for 3 hr and the crude yellow solid was collected in 30% yield (yield was depressed because of the continuous loss of $Cr(CO)_6$ which sublimed from the reaction solution). Sublimation (70°, 0.05 mm) produced pure, bright yellow crystals, mp 73–74°; ν(CO) 1979, 1911 cm^{-1} in hexane. *Anal.* Calcd for $C_{11}H_{10}Cr(CO)_3$: C, 60.43; H, 3.62; Cr, 18.69; O, 17.25; mol wt 278. Found: C, 59.99; H, 3.56; Cr, 18.30; O, 18.85; mol wt 300 (vpo in $CHCl_3$ at 37°) and 278 (mass spectrum). KBr infrared spectra (cm^{-1}): 3070 (w, br), 3045 (w, br), 2967 (w), 2900 (w), ν(CO) bands above, 1462 (sh), 1455 (m), 1428 (s), 1413 (s), 1380 (sh), 1371 (m), 1338 (w), 1318 (m), 1228 (m), 1195 (w), 1182 (w), 1163 (sh), 1157 (s), 1113 (sh), 1082 (m), 1043 (w), 1028 (m), 967 (m), 950 (m), 928 (m), 899 (m), 870 (s), 847 (s), 818 (s), 792 (s), 750 (s), 718 (w), 674 (sh), 668 (s). Carbon-13 spectra (ppm downfield from TMS): 34.3, 91.5, 94.4, 95.1, 105.8, 109.8, 128.3, 130.3, 131.6, 132.4, 234.1.

When $Mo(CO)_6$, $(diglyme)Mo(CO)_3$, $W(CO)_6$, or $(CH_3CN)_3W(CO)_3$ was allowed to react with bcht in both hydrocarbon solvents or neat at temperatures between 25 and 160°, no isolable products could be obtained. Monitoring the metal–carbonyl stretching region indicated only very weak molybdenum product bands and complete decomposition with tungsten.

Results and Discussion

In order to establish methods that might be successful in the synthesis of benzocycloheptatriene complexes, several cycloheptatriene (cht) reactions were attempted with various group VIb metal carbonyl compounds. Those that proved most effective were (1) direct CO replacement in the hexacarbonyls by heating the reaction mixture in hydrocarbon solvents at temperatures between 100 and 132°, (2) replacement of labile groups, CH_3CN or diglyme, in their tricarbonyls in hydrocarbon solvents at temperatures from 60 to 100°, and (3) replacement of labile groups by heating the intermediate with cht in the absence of solvent.

Although the three methods produced the same cht metal

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(1) Part II: T. W. Beall and L. W. Houk, *Inorg. Chem.*, 12, 1979 (1973).

(2) G. R. Dobson, I. W. Stolz, and R. K. Sheline, *Advan. Inorg. Chem. Radiochem.*, 1, 8 (1966).

(3) T. A. Manuel, *Advan. Organometal. Chem.*, 3, 181 (1965).

(4) E. O. Fischer and H. P. Fritz, *Advan. Inorg. Chem. Radiochem.*, 1, 56 (1959).

(5) G. Wilkinson and F. A. Cotton, *Progr. Inorg. Chem.*, 1, 1 (1959).

(6) K. W. Barnett and D. W. Slocum, *J. Organometal. Chem.*, 44, 1 (1972).

(7) M. R. Churchill, *Progr. Inorg. Chem.*, 11, 53 (1970).

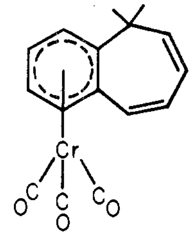
(8) D. J. Bertelli and J. W. Viebrock, *Inorg. Chem.*, 7, 1240 (1968).

(9) J. M. Viebrock, Ph.D. Thesis, University of California at Santa Barbara, Santa Barbara, Calif., 1967.

(10) R. P. M. Werner and T. H. Coffield, *Chem. Ind.* (*London*), 936 (1960).

(11) D. P. Tate, W. R. Knipple, and J. M. Augl, *Inorg. Chem.*, 1, 433 (1962).

tricarbonyls for each of the three group VIb metals, quite different results were observed with bcht. Molybdenum formed only trace amounts of compounds possibly containing the ring, and tungsten led to no reaction complexes of benzocycloheptatriene regardless of the method of synthesis attempted. Reaction of bcht with $Cr(CO)_6$ yielded a yellow product identified as (bcht)$Cr(CO)_3$ based on elemental analyses and molecular weight measurements. Since cycloheptatriene derivatives of group VIb metal carbonyls are red and exhibit three ν(CO) stretching frequencies,[12-14] *e.g.*, for $C_7H_8Cr(CO)_3$, ν(CO) 1991, 1930, 1907 cm^{-1}, and since the frequencies for the yellow benzene metal tricarbonyls[14], *e.g.*, for $C_6H_6Cr(CO)_3$, ν(CO) 1987, 1917 cm^{-1} are quite similar to those for (bcht)$Cr(CO)_3$ (1979, 1911 cm^{-1}), it is proposed that the six-membered ring in bcht is π bonded to the chromium (I). Nonetheless, these results are rather curious in light of the structures of (bcht)$Fe(CO)_3$ and the red phenylcycloheptatrienechromium tricarbonyl $C_6H_5C_7H_7Cr(CO)_3$ (ν(CO) 1989, 1921, 1890 cm^{-1})[12] where exclusive preference for the seven-membered ring is evidenced. (We are grateful to a referee for noting that to coordinate bcht to chromium through the seven-membered ring would require loss of resonance stabilization energy.) Even in the 7,7-dimethoxybenzonorbornadiene and $Cr(CO)_6$ reaction the predominant product does not involve bonding between chromium and the six-membered ring.[15]



I

Although the bcht used in the reactions was composed of two isomers with different methylene proton resonances (1,2-bcht a doublet and 3,4-bcht a triplet),[9] the nmr spectrum of (bcht)$Cr(CO)_3$ exhibited only a doublet at τ 7.00 ($J = 6.0$ Hz). An analogous 3,4 to 1,2 isomer conversion was previously observed in the formation of (bcht)$Fe(CO)_3$.[8] Based on the resonance frequencies in η^6-$C_6H_6Cr(CO)_3$ (τ 4.30)[16] and bcht the three remaining unsymmetrical multiplets were assigned to the four protons on the benzene ring (τ 4.64) and the four vinyl ones on the cycloheptatriene ring (τ 3.96 and 3.33). The proton nmr spectra are completely consistent with π bonding to the six-membered ring in (bcht)$Cr(CO)_3$ and to the seven-membered ring in (bcht)-$Fe(CO)_3$. The vinyl proton resonance in (bcht)$Cr(CO)_3$ is about the same value as that in the free bcht although a marked upfield shift is observed in (bcht)$Fe(CO)_3$. In contrast, the arene protons in (bcht)$Cr(CO)_3$ experienced an upfield shift relative to bcht but they were virtually unchanged in the iron compound. The methylene resonance in both is approximately the same as that in bcht. Carbon-13 resonance values for all the unsaturated ring atoms in (bcht)$Cr(CO)_3$ were shifted upfield from those in benzene,[17] cycloheptatriene,[18] and benzocycloheptatriene; however, the saturated carbon was unaffected.

Table I. Mass Spectra of $C_{11}H_{10}Cr(CO)_3$ and $C_{11}H_{10}$

		Relative Intensities	
m/e	Ion	$C_{11}H_{10}Cr(CO)_3$[b]	$C_{11}H_{10}$[c]
278[a]	$C_{11}H_{10}Cr(CO)_3^+$	88.9	--
250[a]	$C_{11}H_{10}Cr(CO)_2^+$	6.7	--
222[a]	$C_{11}H_{10}CrCO^+$	70.4	--
194[a]	$C_{11}H_{10}Cr^+$	100.0	--
168[a]	$C_9H_8Cr^+$	16.0	--
142	$C_{11}H_{10}^+$	61.2	99.0
141	$C_{11}H_9^+$	76.2	100.0
139	$C_{11}H_{10}Cr(CO)_3^{++}$	14.2	--
128	$C_{10}H_8^+$	4.0	2.0
127	$C_{10}H_7^+$	--	1.3
116	$C_9H_8^+$	8.3	9.3
115	$C_9H_7^+$	62.7	74.0
111[a]	$C_{11}H_{10}CrCO^{++}$	5.2	--
97[a]	$C_{11}H_{10}Cr^{++}$	3.5	--
91	$C_7H_7^+$	1.4	3.1
89	$C_7H_5^+$	6.2	15.0
77	$C_6H_5^+$	5.8	3.8
65	$C_5H_5^+$	1.8	8.2
63	$C_5H_3^+$	5.4	21.0
52[a]	Cr^+	74.6	--

[a] The characteristic pattern for the chromium isotopes was observed for this ion. The m/e value is for the ion containing ^{52}Cr. [b] Run at 85°; other ions (intensities): $C_{11}H_{11}^+$ (8.1), $C_{11}H_8^+$ (1.8), $C_{11}H_7^+$ (14.2), $C_7H_6^+$ (4.1), $C_6H_8^+$ (10.2), $C_5H_6^+$ (12.8), $C_4H_3^+$ (2.0), $C_3H_3^+$ (2.2). [c] Run at 27°; other ions (intensities): $C_{11}H_{11}^+$ (12.0), $C_{11}H_8^+$ (3.7), $C_{11}H_7^+$ (2.7), $C_{10}H_6^+$ (1.8), $C_9H_6^+$ (2.6), $C_9H_5^+$ (5.0), $C_8H_6^+$ (2.5), $C_8H_5^+$ (0.8), $C_8H_2^+$ (1.3), $C_7H_6^+$ (1.6), $C_7H_4^+$ (3.0), $C_7H_3^+$ (4.4), $C_7H_2^+$ (3.7), C_7H^+ (1.3), $C_6H_6^+$ (1.0), $C_6H_4^+$ (3.7), $C_6H_3^+$ (5.4), $C_6H_2^+$ (5.6), $C_{11}H_{11}^{++}$ (1.1), $C_{11}H_{10}^{++}$ (7.8), $C_{11}H_9^{++}$ (10.0), $C_{11}H_8^{++}$ (9.3), $C_{11}H_7^{++}$ (11.0), $C_5H_9^+$ (5.7), $C_5H_4^+$ (2.8), $C_5H_2^+$ (8.1), C_5H^+ (2.1), $C_9H_8^{++}$ (4.7), $C_9H_7^{++}$ (23.0), $C_4H_9^+$ (2.3). Metastable ions: 115.4, $C_{11}H_{10}^+ \rightarrow C_{10}H_8^+ + CH_2$; 114.4, $C_{11}H_9^+ \rightarrow C_{10}H_7^+ + CH_2$; 93.8, $C_{11}H_9^+ \rightarrow C_9H_7^+ + C_2H_2$; 68.9, $C_9H_7^+ \rightarrow C_7H_5^+ \cdot C_2H_2$.

The mass spectral cracking pattern for $C_{11}H_{10}Cr(CO)_3$ (Table I) indicates successive CO loss from the parent ion to produce the most abundant ion $C_{11}H_{10}Cr^+$. Subsequent ring degradation occurs by loss of acetylene to form the $C_9H_8Cr^+$ ion which probably contains indene π-bonded to chromium. Cycloheptatriene ring reduction to cyclopentadiene has been previously documented.[19,20] Small amounts of $C_{10}H_8Cr^+$ were also observed indicating the formation of the naphthalene- or azulenechromium ion. The only other metal-containing ions present were $C_{11}H_{10}Cr(CO)_3^{2+}$, $C_{11}H_{10}CrCO^{2+}$, $C_{11}H_{10}Cr^{2+}$, and Cr^+. Fragmentation of the hydrocarbons seemed to follow benzocycloheptatriene to indene as the major pathway but peaks were observed for ions containing from eleven to three carbon atoms with the exception of eight. The mass spectrum of free benzocycloheptatriene contained metastable peaks and predominant ions suggesting the series of fragmentation reactions

$$C_{11}H_{10}^+ \rightarrow C_{10}H_8^+ + CH_2$$

$$C_{11}H_{10}^+ \rightarrow C_{11}H_9^+ + H$$

$$C_{11}H_9^+ \rightarrow C_{10}H_7^+ + CH_2$$

$$C_{11}H_9^+ \rightarrow C_9H_7^+ + C_2H_2$$

$$C_9H_7^+ \rightarrow C_7H_5^+ + C_2H_2$$

$$C_7H_5^+ \rightarrow C_5H_3^+ + C_2H_2$$

Acknowledgments. We are indebted to the Memphis State University Research Foundation for partial support of this work. We also wish to express our gratitude to Dr. Richard

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(12) E. W. Abel, M. A. Bennett, R. Burton, and G. Wilkinson, *J. Chem. Soc.*, 4559 (1958).

(13) R. B. King and A. Fronzaglia, *Inorg. Chem.*, **5**, 1837 (1966).

(14) R. D. Fischer, *Chem. Ber.*, **93**, 165 (1960).

(15) D. Wege and S. P. Wilkinson, *Aust. J. Chem.*, **26**, 1751 (1973).

(16) N. Hagihara, M. Kumada, and R. Okawara, Ed., "Handbook of Organometallic Compounds," W. A. Benjamin, New York, N. Y., 1968, p 861.

(17) F. J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, **89**, 2967 (1967).

(18) H. Spiesecke and W. G. Schneider, *Tetrahedron Lett.*, 468 (1961).

(19) S. Meyerson, *J. Amer. Chem. Soc.*, **85**, 3340 (1963).

(20) J. Muller and K. Fenderl, *Chem. Ber.*, **103**, 3128 (1970).

Cox of the University of Georgia for running the carbon-13 spectra.

Registry No. $C_{11}H_{10}Cr(CO)_3$, 51731-31-8; bcht, 264-08-4; $Cr(CO)_6$, 13007-92-6.

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Hydrogen Solubility in 1:5 Compounds between Yttrium or Thorium and Nickel or Cobalt

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There is great interest in the hydrogen absorption by metals since hydrogen is a possible candidate for use as a future fuel[1] and since the nature of hydrogen in metals is not well understood.[2] Recently it was found that a number of intermetallic compounds of a rare earth metal and a transition metal absorb large quantities of hydrogen gas at the ambient temperature under moderate pressures (~1-~100 atm) with substantial change in their physical properties.[3,4] Among those intermetallic compounds, $LaNi_5$ is an attractive material for hydrogen storage because of its large hydrogen-holding capacity, its favorable equilibrium pressure, and the rapidity with which it absorbs and releases hydrogen.

Yttrium and the rare earths form similar intermetallic compounds with transition metals. It therefore seemed likely that the yttrium compounds would behave like their rare earth counterparts in respect to hydrogen sorptive power. Because of the lower atomic weight of Y, the yttrium compounds have lower density; this is of significance if the intermetallic is to be used for hydrogen storage in mobile vehicles since weight considerations are then important. In this note we report pressure-composition isotherms for the YCo_5-H system. For purposes of comparison YNi_5, $ThCo_5$, and $ThNi_5$ were also examined as possible solvents for hydrogen.

Intermetallic compounds used were prepared by induction melting in a water-cooled copper boat under an atmosphere of purified argon gas and were homogenized under vacuum at 1000° for 2 weeks to obtain single-phase compounds. Powder X-ray diffraction patterns were obtained to confirm formation of the compounds and to establish the absence of extraneous phases. The lattice constants thus obtained were in good agreement with literature values.

Samples were powdered to fine particles (~75 μ) with a mortar and a pestle in air, then introduced into a brass container, and connected to the hydriding system. Before introducing hydrogen gas (99.999% pure), the whole system was pumped out with a mechanical pump (~10^{-3} mm). Then hydrogen gas was introduced into the system at ~150 atm and pressure was measured with an Ashcroft test gauge. The system was left for some days until the pressure became constant and then evacuated by the mechanical pump. This process was repeated several times before the actual desorption measurements were done.

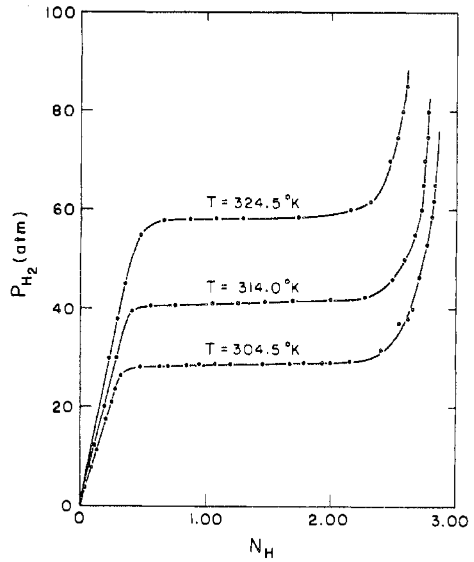

Figure 1. Pressure *vs.* composition for the YCo_5-H system at several temperatures. Composition (N_H) is expressed as the gram-atoms of H per gram formula weight of YCo_5.

YCo_5 and $ThCo_5$ absorb hydrogen gas reversibly giving the limiting composition ratio of hydrogen atom to compound of $N_H \approx 3.0$ in both cases. Pressure-composition isotherms for desorption of the YCo_5-H system at three temperatures are given in Figure 1. These show plateau pressures indicating a two-phase region, *i.e.*, a solid solution and a hydride. The $ThCo_5$-H system has a plateau pressure of 45 atm at 23°. Since this is a rather high pressure for our equipment (maximum pressure is 100 atm for precision measurement), isotherms at higher temperatures were not obtained for the $ThCo_5$-H system. YNi_5 and $ThNi_5$, on the other hand, do not absorb hydrogen gas under the applied pressure of up to 150 atm. This may be due to their high plateau pressure.[3]

After the desorption experiments X-ray powder diffraction patterns of YCo_5 and $ThCo_5$ were taken. The patterns were identical with those obtained before hydriding in each case, indicating no decomposition in either YCo_5 or $ThCo_5$. We had hoped to obtain a crystal structure of the hydride phase, but it was not possible to perform X-ray diffraction measurements on the hydride phase because of the high equilibrium pressure at room temperature.

In Figure 2, log P(atm) *vs.* $1/T$ is plotted for the YCo_5-H system. A linear relation is obtained corresponding to the expression

$$\log P(\text{atm}) = 5.96 - 1679/T$$

From this equation, the heat of reaction to form the hydride is obtained as $\Delta H_f = -7.7$ kcal/mol of H_2,[5] which is very close to that observed in the RCo_5 or RNi_5 systems (R = a rare earth element). For example, $LaNi_5$ and $SmCo_5$ hydrides have heats of reaction of −7.2 kcal/mol of H_2 and −7.4 kcal/mol of H_2, respectively.[3] As stated earlier, the limiting composition N_H is 3 for YCo_5 and $ThCo_5$. This is also the case for most of the RCo_5 or RNi_5 hydrides, *i.e.*, the most stable hydride has the limiting composition $N_H = 3$, although they are known to form several hydride phases.[3]. These findings seem to indicate that the crystal structure is an important factor in the hydrogen absorption by this type of compound. This is also substantiated by the fact that YCo_5, $ThCo_5$, and

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(1) *Chem. Eng. News*, 51, 19 (Sept 10, 1973).

(2) T. R. P. Gibb, Jr., *Progr. Inorg. Chem.*, 3, 315 (1962).

(3) J. H. N. van Vucht, F. A. Kuijpers, and H. C. A. M. Bruning, *Philips Res. Rep.*, 25, 133 (1970).

(4) H. Zijlstra and F. F. Westendorp, *Solid State Commun.*, 7, 857 (1969).

(5) W. M. Mueller, J. P. Blackledge, and G. G. Libowitz, "Metal Hydrides," Academic Press, New York, N. Y., 1968.