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Preliminary communication

RING-OPENING REACTIONS OF SPIRO[2.4]HEPTA-4,6-DIENE AND SPIRO[4.4]NONA-1,3-DIENE WITH $Co_2(CO)_8$; A FACILE ACCESS TO DICARBONYL-η^5-VINYLCYCLOPENTADIENYLCOBALT

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Summary

Spiro[2.4]hepta-4,6-diene and spiro[4.4]nona-1,3-diene both react with $Co_2(CO)_8$, and substituted dicarbonyl-η^5-cyclopentadienylcobalt complexes are formed by disproportionation, coupling, or recyclisation of the ring-opened intermediates.

5,5-Dialkylcyclopentadienes such as spiro[2.4]hepta-4,6-diene (I), spiro[4.4]-nona-1,3-diene (IX) and unstrained open chained analogues are converted into η^5-cyclopentadienyl complexes by metal carbonyls of iron, nickel, molybdenum and tungsten [1]. The metal center is inserted into the carbon—carbon bond of the substrates to form alkylmetal and/or acylmetal systems. Similar transformations have been observed with 1,3-cyclopentadiene [2] and 5-acetyl-1,2,3,4,5-pentamethyl-1,3-cyclopentadiene [3] where a hydrogen atom and acetyl group, respectively, are transferred to the metal center. Stable products of the observed type can only be expected with even atomic numbered transition metal carbonyls. Thus the reaction of cobalt carbonyls with 5,5-dialkylcyclopentadienes yields other products. Increasing interest in substituted η^5-cyclopentadienylcobalt complexes [4] leads us to describe briefly our own work in this field [see refs. 1g,5].

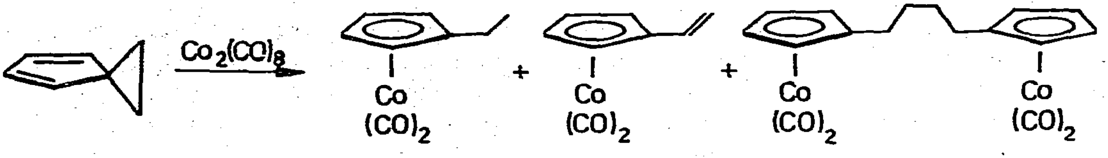
Spiro[2.4]hepta-4,6-diene (I) reacts with $Co_2(CO)_8$ in boiling hexane (65—70°C) under an inert gas or at 100°C under carbon monoxide pressure to form the three dicarbonylcobalt-η^5-cyclopentadienyl systems II, III and IV. Yields were 19, 17 and 19%, respectively, at 65°C and 35, 30 and 7%, respectively, at 100°C. The products were separated by column chromatography and identified by their analyses and spectra (Table 1) and by comparison with other systems of this type [6].

TABLE 1

ANALYTICAL AND SPECTROSCOPIC DATA OF COMPOUNDS II, III, IV, VIII, X, XI, XII[a]

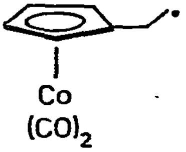
	Elementary analysis (Found (calcd.) (%))		m/e (main fragments) (% rel. int.)	$\tilde{\nu}$(CO) (solvent) (cm^{-1})	δ(C_6D_6) (ppm)
	C	H			
II	52.18 (51.95)	4.42 (4.36)	208 (M^+, 24), 180 (26), 152 (42), 150 (100)	(film): 2020, 1945,	0.92 (t, 3H), 1.91 (q, 2H), 4.43 (~t, 2H), 4.58 (~t, 2H)
III	52.73 (52.45)	3.46 (3.42)	206 (M^+, 24), 178 (29) 150 (100)	(film): 2020, 1950	4.48 (~t, 2H), 4.77 (~t, 2H) 4.87 (dd, 1H), 5.18 (dd, 1H), 6.05 (dd, 1H)
IV	52.71 (52.20)	3.98 (3.89)	386 (M^+ – CO, 40), 358 (22), 328 (56), 300 (100) [FI[c]: 414 (M^+, 100)]	(film): 2010, 1945	0.8-2.5 (m, 8H), 4.57 (mc, 8H)
VIII	51.53 (51.61)	3.53 (3.65)	414 (M^+ – CO, 13), 386, 358, 330, 300, 271, (100)	($CHCl_3$): 2030, 1955, 1710	2.25 (mc, 8H), 4.50 (mc, 8H)
X	56.74 (56.43)	4.73 (4.74)	234 (M^+, 29), 206 (47), 178 (77), 176 (69), 174 (100)	(film): 2015, 1940	1.1-2.4(m, 8H), 4.40 (t, 1H), 4.43 (d, 2H)
XI	[b]		236 (M^+ – CO, 16), 208 (6), 178 (100). [FI[c]: 264 (M^+, 100)]	(film): 2060, 1975	[b]
XII	[b]		FI[c]: 234 (M^+, 100)	(film): 2020, 1950	0.83 (t, 3H), ~2.0 (m, 2H), 4.53 (~t, 2H), 4.63 (~t, 2H), 5.77 (m, 2H)

[a] XI: yellow oil, all other compounds: dark reddish brown oils. [b] Not obtained in analytical purity. [c] Field ionization method.

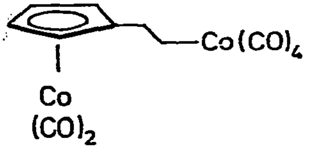


I II III IV

The observed products can have either been formed via a free radical intermediate such as V or an alkylmetal such as VI containing a stable η^5-cyclopentadienyldicarbonylcobalt unit and a reactive $RCo(CO)_4$ unit. Both intermediates can form the observed products by disproportionation and coupling. Preliminary experiments to trap the possible highly reactive alkylmetals under hydrofomylation or hydrocarboxylation conditions were unsuccessful [5].



V

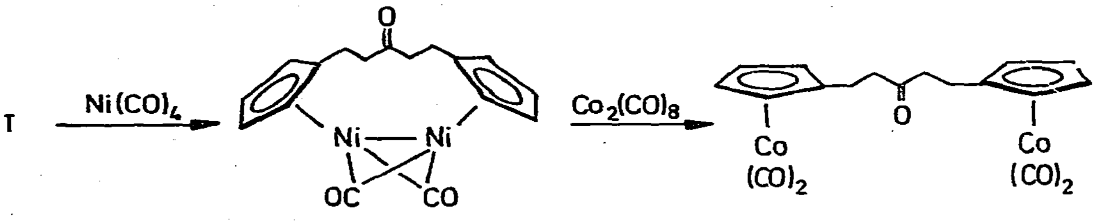


VI

Analogous conversions of the spirodiene I with $Mn_2(CO)_{10}$ leading to similar products were observed [7]. The manganese carbonyl, however, proved to be much less reactive than the cobalt carbonyl and yielded only small amounts of products analogous to II and III.

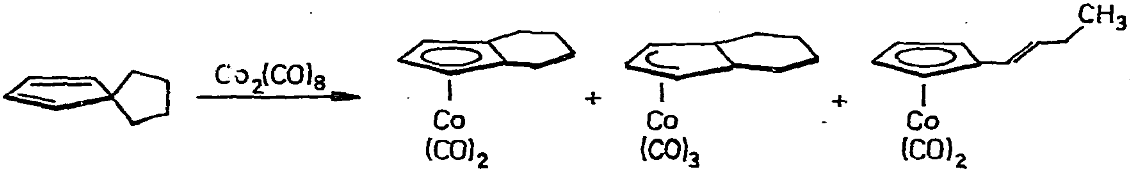
η^5-1-Vinylcyclopentadienyldicarbonylcobalt(III) is of special interest, since it might serve as a monomer for polymer supported η^5-cyclopentadienyldicarbonylcobalt catalysts [8]. Only a few routes to η^5-vinylcyclopentadienyl complexes of cobalt are known [9], and ours seems more convenient.

Interestingly no dinuclear coupling product with CO insertion was found, as was observed with spiroheptadiene (I) and $Ni(CO)_4$ [1b,1k] or in the coupling reactions of alkylcobalt carbonyls [10]. However, if the product of the reaction of I with $Ni(CO)_4$ (VII) is treated with $Co_2(CO)_8$ at elevated temperatures (120°C, CO pressure) the expected complex VIII can be obtained indirectly by ligand exchange in 74% yield (Table 1).



VII VIII

Not only the strained spiroheptadiene I but also the less strained spirononadiene IX react with $Co_2(CO)_8$ in boiling hexane or under CO pressure at 100°C. Several products are formed, but only the η^5-tetrahydroindenyl system X (11%) could be isolated in analytical purity. Other products are tentatively identified as η^3-hexahydroindenyltricarbonylcobalt (XI, 11%) and η^5-butenylcyclopentadienyldicarbonylcobalt (XII) (Table 1). Thus no coupling product could be isolated as in the spiroheptadiene case and recyclization to the tetra- and hexahydroindenyl system seems to dominate over disproportionation.



IX X XI XII

The unstrained 5,5-dimethyl-1,3-cyclopentadiene (XIII) could not be converted into η^5-cyclopentadienyl complexes with $Co_2(CO)_8$. Thus this metal carbonyl turns out to be inactive to CC bond cleavage in substrates of this type, whereas iron, molybdenum and tungsten carbonyls are active [1e,1g,1h,1i].

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