

REACTIONS OF (PROPARGYL)DICOBALT HEXACARBONYL CATIONS WITH METHYLMETALS

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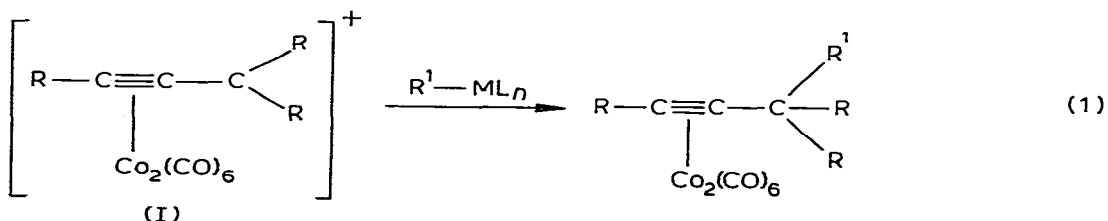
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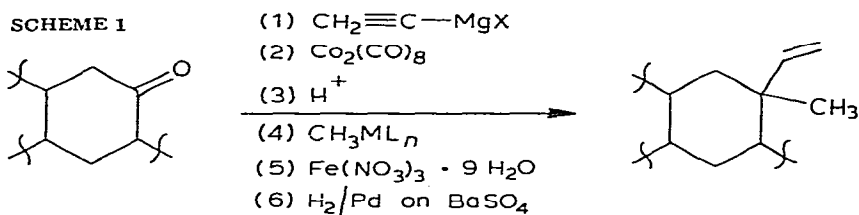
Summary

The reactions of several methyl-metallic compounds, $(\text{CH}_3)\text{ML}_n$ with the cobalt complexes $[(\text{HC}\equiv\text{CCR}^1\text{R}^2)\text{Co}_2(\text{CO})_6]^+\text{BF}_4^-$ (I) and $(\text{HC}\equiv\text{CCR}^1\text{R}^2\text{OAc})\text{Co}_2(\text{CO})_6$ (VIII) have been examined and assessed as a synthetic method for methyl/propargyl coupling. No methyl transfer was observed in the reactions of the cationic complexes I with CH_3MgI , $(\text{CH}_3)_2\text{Cd}$, $(\text{CH}_3)_2\text{Gg}$, $(\text{CH}_3)_4\text{Si}$, $(\text{CH}_3)_4\text{Sn}$ or $(\text{CH}_3)_3\text{SiSi}(\text{CH}_3)_3$ but rather reductively coupled products, $(\text{HC}\equiv\text{CCR}^1\text{R}^2-\text{CR}^1\text{R}^2\text{C}\equiv\text{CH})[\text{Co}_2(\text{CO})_6]_2$ (III), and $(\text{HC}\equiv\text{CCHR}^1\text{R}^2)\text{Co}_2(\text{CO})_6$ (V) were obtained in low yields. Modest yields (5–30%) of methylation products $(\text{HC}\equiv\text{CCR}^1\text{R}^2\text{CH}_3)\text{Co}_2(\text{CO})_6$ (II) were produced from I and $(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{CH}_3$ or $(\text{CH}_3)_3\text{Al}$, accompanied by varying amounts of III. The most efficient route to the methylated derivatives II (25–90% yields) combines the complexed propargyl acetates VIII with $(\text{CH}_3)_3\text{Al}$ under unusually mild conditions (CH_2Cl_2 , -78°C).

As part of a program to explore the organic chemistry and potential synthetic utility of transition metal-stabilized carbonium ions, we have found the propargyl complexes $[(\text{RC}\equiv\text{CCR}_2)\text{Co}_2(\text{CO})_6]^+\text{BF}_4^-$ (I) [1] to be highly reactive and versatile alkylating agents towards a variety of substrates including aromatics [2], β -dicarbonyl compounds [3], ketones and enol derivatives [4], and allyl silanes [5]. To expand the use of these complexes in carbon-carbon bond formation, the development of efficient methods of propargyl/alkyl coupling via reactions of I with nucleophilic organometallics (eq. 1) is of particular interest.



Such reactions would have particular application in the synthesis of natural products including terpenes of the elemene, pimarane, and rosane families [6], which have the generalized structure shown below (Scheme 1).



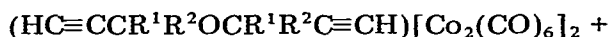
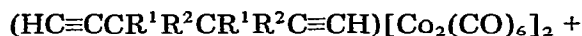
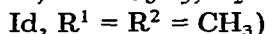
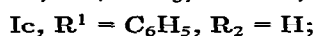
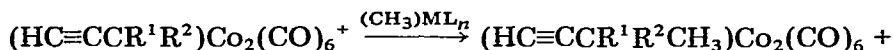
Herein, we describe a study of the interaction of potential methyl transfer agents, CH_3ML_n , with the cations I and propargyl acetate complexes $(\text{RC}\equiv\text{CCR}_2\text{OAc})\text{Co}_2(\text{CO})_6$ (VIII) which has led to a selective propargyl/methyl coupling method free of the usual limitations of allenic isomerism encountered with conventional propargyl/alkyl coupling [7].

While there has been an ever increasing number of synthetically useful C—C bond-forming reactions based on the electrophilic cleavage of alkyl-, vinyl-, and aryl-metallic species [8], reports of simple alkyl transfer from metal alkyls to stable carbocations or metal-stabilized carbocations are scarce. Notable examples include the reactions of dialkylcadmiums and cuprates with (allyl) $\text{Fe}(\text{CO})_4^+$ [9] and (pentadienyl) $\text{Fe}(\text{CO})_3^+$ [10] complexes, $(\text{CH}_3)_4\text{Sn}$ with the cluster acylium ion $[(\text{CO})_9\text{Co}_3\text{CCO}]^+$ [11], and RMgX and RLi with α -ferrocenyl carbonium ions [12]. Also of relevance are the reactions of diaryl and triarylcabinols [13], alkyl halides [14], and benzylic, allylic and cyclopropylcarbinyl acetates [15] with trialkylaluminiums, which appear to proceed via carbocationic intermediates.

Results and discussion

In initial survey studies the simple propargyl complex $(\text{HC}\equiv\text{CCH}_2)\text{Co}_2(\text{CO})_6^+-\text{BF}_4^-$ (Ia) was combined with the readily available metal methyls CH_3MgI , $(\text{CH}_3)_2\text{Cd}$, $(\text{CH}_3)_2\text{Hg}$, $(\text{CH}_3)_4\text{Si}$, $(\text{CH}_3)_3\text{SiSi}(\text{CH}_3)_3$, $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_3$, and $(\text{CH}_3)_3\text{Al}$. Where methyl transfer occurred, the substituted complexes Ib—Id were also examined. Ether or methylene chloride were selected as solvents depending on the tolerability of the metal alkyl towards the latter. Reactions were initiated at -78°C , monitored by TLC, and warmed to room temperature if necessary to maintain a reasonable reaction rate (for the Hg, Si, Sn, and Fe methyls). Generally, no precautions were taken to preclude hydrolysis during workup. Unreacted salts I and the corresponding alcohols from hydrolysis were retained on alumina upon workup, accounting for the modest mass recoveries in several instances. The organocobalt products were separated by chromatography on silica and identified by IR, ^1H NMR, and comparison with authentic samples.

Four types of cobalt-acetylene complexes were characterized as products of these reactions (eq. 2): 1) The methylated complexes $(\text{HC}\equiv\text{CCR}^1\text{R}^2\text{CH}_3)\text{Co}_2(\text{CO})_6$ (II); 2) dimeric complexes, $(\text{HC}\equiv\text{CCR}^1\text{R}^2-\text{CR}^1\text{R}^2\text{C}\equiv\text{CH})[\text{Co}_2(\text{CO})_6]_2$ (III); 3) ether complexes, $(\text{HC}\equiv\text{CCR}^1\text{R}^2\text{OCR}^1\text{R}^2\text{C}\equiv\text{CH})[\text{Co}_2(\text{CO})_6]_2$ (IV); 4) reduction products, $(\text{HC}\equiv\text{CCHR}^1\text{R}^2)\text{Co}_2(\text{CO})_6$ (V).



No methylation products II were obtained in reactions with CH_3MgI , $(\text{CH}_3)_2\text{Cd}$ (with Ia or Ic), $(\text{CH}_3)_2\text{Hg}$, $(\text{CH}_3)_4\text{Si}$, $(\text{CH}_3)_4\text{Sn}$ or $(\text{CH}_3)_6\text{Si}_2$. It appears that no productive interaction with $(\text{CH}_3)_2\text{Hg}$ (20°C /ether/3 h) occurs since only the ether complex IVa was isolated (21%), arising from partial hydrolysis of unreacted Ia during workup. Reactions with the Si and Sn reagents were quite sluggish at room temperature; after 1–2 days, the major product complex proved to be the dimeric species IIIa (6–33%) accompanied by trace amounts of $(\text{HC}\equiv\text{CCH}_3)\text{Co}_2(\text{CO})_6$ (V). The H-source for the formation of V was not determined.



The active involvement of the metal alkyls in these reactions seems indicated by the much slower (but detectable) production of IIIa and V in CH_2Cl_2 alone (3% IIIa after 4 days). As anticipated, reactions of I with CH_3MgI and $(\text{CH}_3)_2\text{Cd}$ were more rapid, being essentially complete at -78°C within minutes. Here again, the coupled products III dominated, (product, reagent, % yield): (IIIa, CH_3MgI , 20%); (IIIa, $(\text{CH}_3)_2\text{Cd}$, 24%); and (IIIc, $(\text{CH}_3)_2\text{Cd}$, 45%).

Formation of the dimers III and propyne complex Va strongly suggests the intermediacy of radical VI derived from one electron reduction of I (eq. 4) by metal alkyl.



Several recent studies have implicated similar electron transfer processes in electrophilic cleavages of metal alkyls [16]. Single electron reductions of stable carbonium ions including trityl [17], tropylium [18], cyclopropenyl [19], and α -ferrocenyl methyl [20] also are well documented.

Our first encouraging results were obtained using $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_3$ as the methyl transfer agent. Reactions with cations Ia–Id in CH_2Cl_2 at room tempera-

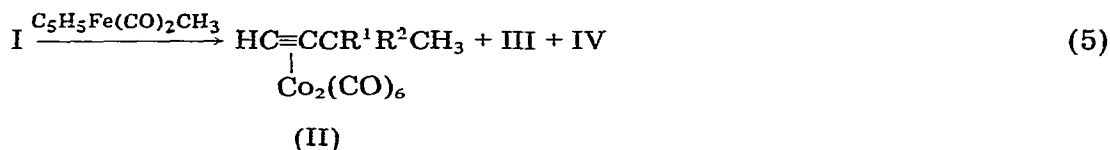
TABLE 1

METHYLATION OF $[(HC\equiv CCR^1R^2)Co_2(CO)_6]^+BF_4^-$ (I) BY $(C_5H_5)Fe(CO)_2CH_3$ AND $(CH_3)_3Al$

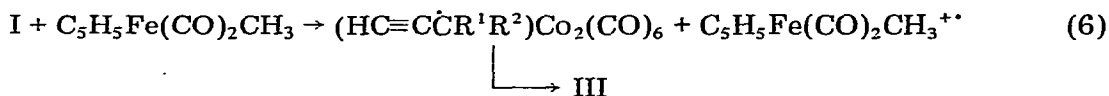
Complex	Methylating agent	Yield of products (%)	
		II	III
Ia	$C_5H_5Fe(CO)_2CH_3$	20	22 ^a
Ib	$C_4H_5Fe(CO)_2CH_3$	21	17 ^b
Ic	$C_5H_5Fe(CO)_2CH_3$	17	22
Id	$C_5H_5Fe(CO)_2CH_3$	5	— ^b
Ic	$(CH_3)_3Al$	25	24
Ic	$(CH_3)_3Al$	38	12

^a 12% ether IVa also obtained. ^b Some $C_5H_5Fe(CO)_2CH_3$ recovered.

ture for 3–8 h, followed by solvent removal and chromatography afforded the methylated products IIa–IIId in low yields as well as the previously encountered dimers III and ethers IV (eq. 5, and Table 1). The iron containing product(s) was not determined.



Despite the low yields, the generality of the reaction and particularly the methyl transfer to the tertiary cation Id are noteworthy features. While electrophilic cleavage reactions of $C_5H_5Fe(CO)_2(alkyl)$ complexes have been widely studied, this appears to be the first report of iron–carbon scission by a carbon electrophile. Formation of dimers III again points to electron-transfer oxidation of the metal alkyl by cation I (eq. 6).



Similar one-electron oxidation mechanisms have been proposed in cleavages of $C_5H_5Fe(CO)_2R$ by halogens [21], $CuCl_2$ [22a, b], $(NH_4)_2Ce(NO_3)_6$ [23], and electrochemically [22b]. Whether formation of methylated products II proceeds by direct S_E2 reaction or rather via an initial redox reaction followed by alkyl transfer from the radical cation cannot be determined at this time.

Trimethylaluminum proved to be a somewhat more efficient methylating agent of the cations than the iron methyl (Table 1). Cation Ic reacted rapidly with $(CH_3)_3Al$ at $-78^\circ C$ in CH_2Cl_2 to give after hydrolytic workup and chromatography moderate yields of IIc as well as dimer IIIc. The methylation/dimerization ratio was improved somewhat by adding the cation salt portionswise to the $(CH_3)_3Al$ solution, presumably having the effect of diminishing local building up of radical VI.

This modest success coupled with the previously mentioned reports of alkylation by alkyl aluminums of activated alcohols and acetates prompted us to examine the interaction of the corresponding propargyl alcohol and acetate

unknown whether the methylated products arise from concerted methyl transfer to the cation I generated by Al-assisted acetate abstraction or from reduction to the radicals VI followed by methyl delivery. Finally, it was found that methylation could be enhanced at the expense of reductive dimerization for VIIIa and VIIIb by slowly adding acetate complex in CH_2Cl_2 to $(\text{CH}_3)_3\text{Al}$ in the same solvent at -78°C (see Table 2).

While future improvements in efficiency are anticipated, we plan to explore synthetic applications of the propargyl/methyl coupling reactions of (propargyl acetate) $\text{Co}_2(\text{CO})_6$ complexes with $(\text{CH}_3)_3\text{Al}$, particularly in generating quaternary centers. Extension to other aluminum alkyls and aryls is also anticipated.

Experimental

Spectra were obtained on the following instruments: (1) infrared: Perkin-Elmer 137 and 599B spectrometers; (2) NMR: at 60 MHz on Hitachi Perkin-Elmer R-24 and at 80 MHz on Varian FT-80A spectrometers. Elemental analyses were performed by Galbraith Laboratories.

Trimethylaluminum was used as a 2 M solution in toluene (Aldrich Chemical Co.). σ -Methyl- π -cyclopentadienyliron dicarbonyl was prepared by the method of King [25]. The alcohol and cationic complexes of dicobalt hexacarbonyl were prepared as previously described [1]. Methylene chloride was dried by distillation from calcium hydride. All manipulations of organometallic compounds were carried out under a nitrogen atmosphere.

Reaction of Ia with $(\text{CH}_3)_2\text{Hg}$, $(\text{CH}_3)_4\text{Si}$, $(\text{CH}_3)_4\text{Sn}$, and $(\text{CH}_3)_6\text{Si}_2$

The following general procedure was employed for the reactions above. To a stirred solution of the metal alkyl (1.0 mmol) in 20 ml CH_2Cl_2 at -78°C was added the solid cobalt salt (1.0 mmol). TLC monitoring indicated no appreciable reactions at -78°C , so the mixtures were allowed to warm to room temperature and concluded at the indicated times — Hg (4 h), Si (72 h), Sn (48 h), Si_2 (17 h). The reaction mixtures were filtered through a bed of Celite and alumina (removing unreacted cobalt salt) and the concentrated residues chromatographed (preparative TLC) over silica gel. Development with petroleum ether afforded the product complexes IIIa, IVa, and Va. Yields and physical properties are given below.

TABLE 3
PRODUCTS FROM REACTIONS OF Ia WITH $(\text{CH}_3)_2\text{Hg}$, $(\text{CH}_3)_4\text{Si}$, $(\text{CH}_3)_4\text{Sn}$ AND $(\text{CH}_3)_6\text{Si}_2$

Complex	CH_3ML_n	Products (% yield)		
		IIIa	IVa ^a	Va
Ia	$(\text{CH}_3)_2\text{Hg}$	—	21	—
Ia	$(\text{CH}_3)_4\text{Si}$	7	—	21
Ia	$(\text{CH}_3)_4\text{Sn}$	33	—	1
Ia	$(\text{CH}_3)_6\text{Si}_2$	11	—	2

^a Extent of ether formation (IV) was dependent on care exercised to exclude moisture during workup.

($HC\equiv CCH_2CH_2C\equiv CH$)[$Co_2(CO)_6$] $_2$ (IIIa). Identical in all respects to an authentic sample prepared from 1,5-hexadiyne and excess $Co_2(CO)_8$; m.p. $80^\circ C$ (dec); IR (CS_2): 2100, 2050, 2020 cm^{-1} (metal carbonyl); NMR (CS_2): δ 3.15 (s, 4 H), 5.95 ppm (s, 2 H).

($HC\equiv CCH_2OCH_2C\equiv CH$)[$Co_2(CO)_6$] $_2$ (IVa). m.p. $65^\circ C$ (dec); IR (CS_2): 2100, 2050, 2020 cm^{-1} (metal carbonyl); NMR (CS_2): δ 4.8 (s, 4 H), 6.0 ppm (s, 2 H); Anal. Found: C, 32.58; H, 0.96. $C_{18}H_6Co_2O_{13}$ calcd.: C, 32.46; H, 0.91%.

($HC\equiv CCH_3$) $Co_2(CO)_6$ (Va). identical to an authentic sample from propyne and $Co_2(CO)_8$; red oil; IR (CS_2): 2095, 2040, 2015 cm^{-1} (metal carbonyl); NMR (CS_2): δ 2.65 (s, 3 H), 5.8 ppm (s, 1 H); lit. [27] δ 2.6, 5.8 ppm.

Reactions of Ia and Ic with CH_3MgI and $(CH_3)_2Cd$

To a stirred solution of the Grignard or cadmium reagent [26] (1.0 mmol) in 20 ml of dry ether at $-78^\circ C$ was added 1.0 mmol of Ia or Ic. After stirring at $-78^\circ C$ for 30–75 min, the mixture was extracted with ice-cold saturated NH_4Cl solution (2×50 ml) and then with water (2×50 ml). The dried ether layer was concentrated and chromatographed (TLC) on silica to yield the products given in Table 4.

($HC\equiv CCHPh-CHPhC\equiv CH$) [$Co_2(CO)_6$] $_2$ (IIIc). m.p. $138-140^\circ C$; IR (CS_2): 2090, 2040, 2015 cm^{-1} (metal carbonyl); NMR (CS_2): δ 4.25 (s, 2 H), 6.1 (s, 2 H), 6.9 ppm (s, 10 H); Anal. Found: C, 45.23; H, 2.05. $C_{30}H_{14}Co_2O_{12}$ calcd.: C, 44.93; H, 1.75%.

($HC\equiv CCHPhOCHPhC\equiv CH$)[$Co_2(CO)_6$] $_2$ (IVc). contaminated with IIIc; IR (CS_2): 2095, 2045, 2025 cm^{-1} (metal carbonyl); NMR (CS_2): δ 5.55 (s, 2 H), 6.05 (s, 2 H), 7.4 ppm (s, 10 H).

Reaction of Ia–Id with $C_5H_5Fe(CO)_2CH_3$

The following general procedure was employed: To a stirred solution of $C_5H_5Fe(CO)_2CH_3$ (1.0 mmol) in 40 ml dry CH_2Cl_2 at $-78^\circ C$ was added the cation complex I (1.0 mmol) in one lot. After stirring at $-78^\circ C$ for one hour and 4–8 h at $20^\circ C$, the reaction mixture was filtered through celite/alumina and concentrated to afford a red oil. Preparative TLC over silica gel employing petroleum ether for development gave the product distributions presented in Table 1.

Spectroscopic and analytical data are as follows.

IIa. red liquid; IR (CS_2): 2095, 2045, 2025 cm^{-1} ; NMR (CS_2): δ 1.3 (t, 3 H),

TABLE 4

PRODUCTS FROM REACTION OF Ia AND Ic WITH CH_3MgI AND $(CH_3)_2Cd$

Complex	CH_3MLn	IIIa (%)	IIIc (%)	IVc (%)
Ia	CH_3MgI	20	—	—
Ia	$(CH_3)_2Cd$	21	—	—
Ic	$(CH_3)_2Cd$	—	45 ^a	35 ^a

^a Estimated by NMR; inseparable by preparative TLC. A pure sample of IIIc for analysis was obtained from Ic + $CpFe(CO)_2CH_3$ (vide infra).

2.9 (q, 3 H), 5.95 ppm (s, 1 H); Anal. Found: C, 35.41; H, 1.84. $C_{10}H_6Co_2O_6$ calcd.: C, 35.32; H, 1.77%.

Iib. red liquid; IR (CS_2): 2095, 2045, 2020 cm^{-1} ; NMR (CS_3): δ 1.1 (d, 6 H), 2.8 (m, 1 H), 5.75 ppm (s, 1 H); lit. [28] δ 1.1, 2.7, 5.7 ppm.

IIIb. m.p. 85°C; IR (CS_2): 2090, 2050, 2025 cm^{-1} ; NMR (CS_2): δ 1.1 (d, 6 H), 3.0 (m, 2 H), 5.85 ppm (s, 2 H); Anal. Found: C, 35.38; H, 2.05 $C_{20}H_{10}Co_4O_{12}$ calcd.: C, 35.43; H, 1.49%.

Iic. red oil; IR (CS_2): 2095, 2045, 2020 cm^{-1} ; NMR (CS_2): δ 1.55 (d, 3 H), 3.95 (q, 1 H), 5.8 (s, 1 H), 7.0 ppm (s, 5 H); Anal. Found: C, 46.46; H, 2.46. $C_{16}H_{10}Co_2O_6$ calcd.: C, 46.18; H, 2.43%.

Iid. red oil; IR (CS_2): 2090, 2040, 2010 cm^{-1} ; NMR (CS_2): δ 1.28 (s, 9 H), 6.01 ppm (s, 1 H); Anal. Found: C, 39.38; H, 2.98. $C_{11}H_8Co_2O_6$ calcd.: C, 39.15; H, 2.74%.

Reaction of Ic with $(CH_3)_3Al$

To a stirred solution of 0.49 g (1.0 mmol) of cation complex Ic in 20 ml of dry CH_2Cl_2 at $-78^\circ C$ was added 1.5 ml (3.0 mmol) of $(CH_3)_3Al$. After stirring at this temperature for 1 h, ether (50 ml) was added and the reddish-brown organic layer was washed with saturated NH_4Cl (2×50 ml) and water (2×50 ml). The dried ether layer on evaporation furnished a crude brown gummy solid. Preparative TLC over silica gel (petroleum ether eluant) furnished two products: the methylated complex Iic (0.10 g, 25%) and the dimer IIIc (0.09 g, 24%).

Inverse addition. The cation complex (Ic) (0.49 g, 1 mmol) was added in small quantities to $(CH_3)_3Al$ (1.5 ml, 3.0 mmol) in CH_2Cl_2 (20 ml) at $-78^\circ C$. After the usual work-up, a mixture (0.13 g) of the methylated complex Iic and the dimer IIIc was obtained. Calculation from the NMR spectrum of the mixture indicated yields of 38% of Iic and 12% of IIIc.

Reaction of VIIc with $(CH_3)_3Al$

To a stirred solution of 0.49 g (1.0 mmol) of the alcohol complex VIIc in 20 ml dry toluene at $-78^\circ C$ was added 1.5 ml (3.0 mmol) of $(CH_3)_3Al$ (2 M in toluene). The reddish reaction mixture was stirred at $-78^\circ C$ for 1 h and after stirring for an additional 12 h at room temperature, saturated NH_4Cl solution was added and the aqueous layer extracted with ether (2×50 ml). The combined organic layer was washed with water (2×50 ml) and dried. Evaporation of the ether furnished a red solid (0.37 g) identified as starting alcohol complex, VIIc (75%) by comparative TLC and NMR.

Preparation of (propargyl acetate)dicobalt hexacarbonyl complexes

The following generalized procedure was employed: To a solution of the propargyl alcohol complex VIIa–VIIc (10 mmol) in 25 ml CH_2Cl_2 was added acetic anhydride (200 mmol) and a catalytic amount of pyridine and the reaction mixture stirred for 3 h. Excess acetic anhydride and CH_2Cl_2 were then distilled under vacuum. The residue was taken up in ether and extracted with saturated $NaHCO_3$ solution (2×50 ml) and then with water (2×50 ml). The ether solution was dried over anhydrous magnesium sulfate and solvent evaporated whereby the pure complexes were obtained as red oils. Analytically pure samples were obtained by chromatography over silica gel. For the preparation of

the acetate of (3-methyl-1-butyne-3-ol)dicobalt hexacarbonyl the general procedure of Hofle [24] was adapted as follows: A mixture of VIId (0.76 g, 2.0 mmol), triethylamine (0.6 g, 4.0 mmol), acetic anhydride (0.8 g, 8.0 mmol) and 4-dimethylaminopyridine (0.22 g, 1.0 mmol) in 20 ml CH_2Cl_2 was stirred for 30 h at room temperature. The solution was partitioned between ether and 2 *N* HCl, the organic phase washed with saturated NaHCO_3 solution (2 \times 50 ml), dried and evaporated to afford VIId as dark red oil, pure by ^1H NMR (below). Attempts to obtain an analytical sample of VIId were frustrated by its facile elimination of HOAc.

Physical and analytical data for the acetate complexes are provided below, yields are in parenthesis.

VIIIa. (92%); IR (CS_2): 2100, 2050, 2030 (metal carbonyl), 1750 cm^{-1} ; NMR (CS_2): δ 2.0 (s, 3 H), 5.15 (s, 2 H), 5.95 ppm (s, 1 H). Found: C, 34.34; H, 1.64. Anal. $\text{C}_{11}\text{H}_6\text{Co}_2\text{O}_8$ calcd.: C, 34.41; H, 1.57%.

VIIIb. (88%); IR (CS_2): 20.95, 2050, 2020 (metal carbonyl), 1740 cm^{-1} ; NMR (CS_2): δ 1.45 (d, 3 H), 1.95 (s, 3 H), 5.95 (q, 1 H), 5.85 ppm (s, 1 H). Anal. Found: C, 36.37; H, 2.16. $\text{C}_{12}\text{H}_8\text{Co}_2\text{O}_8$ calcd.: C, 36.31; H, 2.03%.

VIIIc. (97%); IR (CS_2): 2090, 2050, 2020 (metal carbonyl), 1740 cm^{-1} ; NMR (CS_2): δ 2.09 (s, 3 H), 5.35 (s, 1 H), 6.8 (s, 1 H), 7.15 ppm (s, 5 H). Anal. Found: C, 44.37; H, 2.19. $\text{C}_{17}\text{H}_{10}\text{Co}_2\text{O}_8$ calcd.: C, 44.38; H, 2.19%.

VIIId. (76%); IR (CS_2): 2095, 2040, 2020 (metal carbonyl), 1740 cm^{-1} ; NMR (CDCl_3): δ 1.81 (s, 6 H), 1.97 (s, 3 H), 6.05 ppm (s, 1 H).

Reaction of VIIIa with $(\text{CH}_3)_3\text{Al}$

To a stirred solution of acetate complex VIIIa (0.60 g, 1.6 mmol) in 20 ml CH_2Cl_2 at -78°C was added 3.0 ml (6.0 mmol) of $(\text{CH}_3)_3\text{Al}$ and stirred at -78°C for 25 min. Work-up and purification as described for VIIc furnished two products; methylated complex IIa (0.04 g, 10%) and dimer IIIa (0.15 g, 29%).

Inverse addition. Repetition of the above reaction by adding a CH_2Cl_2 solution of the acetate complex (1.2 g, 3.2 mmol) in small quantities to $(\text{CH}_3)_3\text{Al}$ (9.0 ml, 18.0 mmol) in CH_2Cl_2 at -78°C and stirring for 35 min furnished exclusively the methylated complex IIa (0.45 g, 51%) following the usual work-up.

Reaction of VIIId with $(\text{CH}_3)_3\text{Al}$

Following the usual procedure and a reaction time of 30 min two products were obtained: the methylated complex IIb (20%) and dimer IIIb (26%).

Inverse addition. Repetition of the above reaction by adding a solution of the acetate IIIb (2.3 g, 6.0 mmol) in small quantities to $(\text{CH}_3)_3\text{Al}$ (18.0 ml, 36.0 mmol) at -78°C and stirring for 40 min furnished a mixture of the methylated complex IIb and the dimer IIIb. Calculation from the NMR spectrum of the mixture indicated a 25% yield of IIb and 22% of IIIb.

Reaction of VIIIc with $(\text{CH}_3)_3\text{Al}$

Following the standard procedure and a reaction time of 5 min at -78°C gave exclusively the methylated complex IIc (91%).

Reaction of VIIIId with (CH₃)₃Al

Following the standard procedure after 30 min at -78°C , a single product was isolated, methylated complex IId (45%).

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