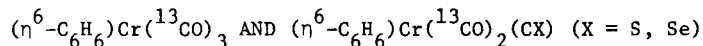


REACTIONS OF METAL CARBONYL COMPLEXES. XII*.

SYNTHESIS OF ^{13}C -LABELLED (η^6 -BENZENE)CHROMIUM(0) CHALCOCARBONYL COMPLEXES:

Ann M. English, Keith R. Plowman[†], and Ian S. Butler
 Department of Chemistry, McGill University, 801 Sherbrooke St. West,
 Montreal, Quebec, Canada H3A 2K6

SUMMARY

^{13}C -Labelled (η^6 -benzene)tricarbonylchromium(0), $\text{BzCr}(^{13}\text{CO})_3$ ($\text{Bz} = \eta^6\text{-C}_6\text{H}_6$), has been prepared in about 50% yield with greater than 90 atom% ^{13}C -enrichment by a multistep, photochemically-induced exchange of the three carbonyl groups in $\text{BzCr}(\text{CO})_3$ with ^{13}CO . The syntheses of the closely related, ^{13}CO -labelled, thiocarbonyl and selenocarbonyl derivatives, $\text{BzCr}(^{13}\text{CO})_2(\text{CX})$ ($\text{X} = \text{S, Se}$), from $\text{BzCr}(^{13}\text{CO})_3$ are also described.

Key words: Chromium Complexes, Carbonyl, Thiocarbonyl, Selenocarbonyl

INTRODUCTION

For many years, we have been interested in the vibrational spectra of transition metal carbonyl complexes, e.g., $\text{trans-W}(\text{CO})_4(\text{NO})\text{Br}$,¹ $\text{CpMn}(\text{CO})_2(\text{CS})$ and $\text{CpMn}(\text{CO})(\text{CS})_2$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$),² and $\text{W}(\text{CO})_5(\text{CS})$.³ In order to assign the infrared and Raman spectra of these molecules, it is often necessary to resort to detailed normal coordinate analyses and isotopic data are essential for such calculations. The easiest way to label metal carbonyls is through CO exchange reactions using either ^{13}CO or C^{18}O , both of which are readily available in high isotopic enrichment. We report here the synthesis of $\text{BzCr}(^{13}\text{CO})_3$ ($\text{Bz} = \eta^6\text{-C}_6\text{H}_6$) by a general procedure which could be used to label the CO groups of many other metal carbonyl complexes that undergo thermal or photochemical CO exchange.

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[†]Present address: Dow Chemical Co., Baton Rouge, Louisiana, U.S.A.

In addition, the synthesis of the closely related molecules, $\text{BzCr}({}^{13}\text{CO})_2(\text{CX})$ ($\text{X} = \text{S}, \text{Se}$), is also described. The three isotopically labelled derivatives were needed to perform a detailed vibrational analysis for $\text{BzCr}(\text{CO})_3$ and $\text{BzCr}(\text{CO})_2(\text{CX})$, the main point of interest being a comparison of the bonding properties of the chalcocarbonyl ligands, CO, CS, and CSe.

Approximately 90 atom% ${}^{13}\text{C}$ -enrichment of the CO groups in $\text{BzCr}(\text{CO})_3$ and $\text{BzCr}(\text{CO})_2(\text{CX})$ was desired since high concentrations of partially labelled species would complicate the vibrational spectra, especially in the low energy region ($700\text{--}300\text{ cm}^{-1}$) where weak and overlapping bands are usually present. Substitution of the CO groups in $\text{BzCr}(\text{CO})_3$ should be carried out photochemically since thermal reactions only lead to arene group replacement with no loss of CO.⁴ Thus, the most convenient route to $\text{BzCr}({}^{13}\text{CO})_3$ is the photochemically-induced exchange of the three CO groups in the unlabelled molecule with ${}^{13}\text{CO}$. The best method to prepare the $\text{BzCr}({}^{13}\text{CO})_2(\text{CX})$ derivatives is not, however, direct photochemical exchange with ${}^{13}\text{CO}$ because ultraviolet irradiation of the $\text{BzCr}(\text{CO})_2(\text{CX})$ complexes leads to extensive decomposition. The preferred route is the replacement of one of the ${}^{13}\text{CO}$ groups in $\text{BzCr}({}^{13}\text{CO})_3$ with CX according to the literature procedures^{5,6} after the desired isotopic enrichment has been achieved.

Since we needed $\text{BzCr}({}^{13}\text{CO})_3$ as a precursor for further synthesis as well as for vibrational analysis, we decided to prepare approximately 1 g of the ${}^{13}\text{C}$ -labelled complex. To obtain this quantity with 90 atom% ${}^{13}\text{C}$ -enrichment from a single-step exchange reaction would require about 6 l of 95 atom% ${}^{13}\text{CO}$ [at a current cost of ca. \$160. (U.S.) per liter] and there would be about 6 l of 90 atom% ${}^{13}\text{CO}$ remaining after the reaction. A much less expensive procedure would be to enrich the starting material in several steps. The quantity of $\text{BzCr}(\text{CO})_3$ to be enriched is divided among several reaction vessels. Then, ${}^{13}\text{CO}$ (95 atom%) is introduced in a 5:1 molar ratio into reaction vessel #1 and photochemically-induced CO exchange is performed until equilibrium is reached. The CO gas of reduced atom% ${}^{13}\text{C}$ content is removed and transferred to reaction vessel #2

while reaction vessel #1 is charged with a fresh supply of 95 atom% ^{13}C . Both vessels are then subjected to ultraviolet irradiation until the exchange reactions reach equilibrium. This procedure is continued until the exchange reactions in all of the reaction vessels have been completed. Table I summarizes the statistical equilibration expected for each step for five reaction vessels using a 5:1 molar ratio of ^{13}C to $\text{BzCr}(\text{CO})_3$. Theoretically, under these conditions, 1.5 g of $\text{BzCr}(^{13}\text{C})_3$ with 90 atom% ^{13}C -enrichment should be produced from 1 l of 95 atom% ^{13}C ; the CO recovered after the multistep exchange reaction should be depleted to about 50 atom% ^{13}C -enrichment.

Table 1. Atom Fraction of ^{13}C in Reaction Vessels #1-5 after Statistical Equilibration for a 5:1 Molar Ratio of ^{13}C to $\text{BzCr}(\text{CO})_3$ *

Reaction Step (1 step = 8 h irradiation)	Reaction Vessel				
	1	2	3	4	5
1	S → 0.594	-	-	-	-
2	S → 0.816	↘ 0.371	-	-	-
3	S → 0.900	↘ 0.649	↘ 0.232	-	-
4		↘ 0.806	↘ 0.493	↘ 0.145	-
5		S → 0.896	↘ 0.689	↘ 0.362	↘ 0.091 → R
6			↘ 0.816	↘ 0.566	↘ 0.260 → R
7			S → 0.900	↘ 0.722	↘ 0.451 → R
8				↘ 0.833	↘ 0.620 → R
9				S → 0.906	↘ 0.753 → R
10					↘ 0.849 → R

*Arrows indicate pathways of ^{13}C transferral from vessel to vessel. S = supply vessel; R = recovery vessel.

EXPERIMENTAL

Carbon monoxide gas (95 atom% ^{13}C -enriched) was purchased from Prochem (Deer Park Road, London SW193UF, England). The $\text{BzCr}(\text{CO})_3$ complex was prepared by Rausch's method:⁷ $\text{Cr}(\text{CO})_6$ (12 g; Alfa Products, Danvers, Massachusetts, U.S.A.) was dissolved in a mixture of benzene (120 mL) and 2-picoline (75 mL). After refluxing this mixture for 1 week, the tricarbonyl product was extracted with

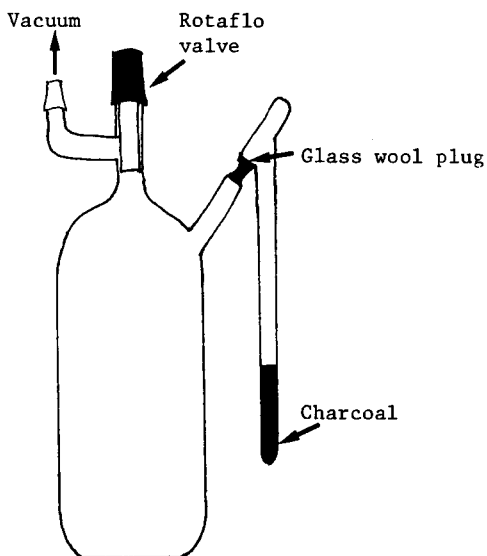


Figure 1. Typical Reaction Vessel for CO Exchange Reactions

diethyl ether and recrystallized from diethyl ether/hexanes (8.8 g, 75% yield; mp 163-164°C, lit.⁷ 162-163°C). All solvents were dried and distilled under nitrogen prior to use. Infrared spectra were recorded on a Perkin-Elmer 521 grating spectrophotometer; the $\nu(\text{CO})$ bands reported were calibrated against standard bands of polystyrene and CO gas, and are considered to be accurate to $\pm 0.5 \text{ cm}^{-1}$.

Preparation of $\text{BzCr}(\text{}^{13}\text{CO})_3$. A sketch of a typical reaction vessel is shown in Figure 1. Five such vessels were constructed and attached to a calibrated vacuum manifold; the capacity of each vessel was $\sim 100 \text{ mL}$. Supply and recovery vessels (capacity $\sim 250 \text{ mL}$) for the ^{13}CO gas were also connected to the vacuum line. Several grams of activated charcoal were placed in each vessel to allow quantitative transfer of ^{13}CO from vessel to vessel. The volume of gas transferred each time was completely adsorbed onto the charcoal at -196°C ; in the absence of charcoal, complete transfer of ^{13}CO from vessel to vessel was not possible because the gas has a vapor pressure of 400 torr at -196°C .⁸ The ultraviolet source used for the irradiations was a 100 W Hanovia-type, mercury-vapor lamp (No. 6515-30; Ace Glass Inc., Vineland, New Jersey, U.S.A.).

Approximately 300 mg of $\text{BzCr}(\text{CO})_3$ was dissolved in 90 mL of tetrahydrofuran and the solution was placed in reaction vessel #1. This vessel was re-connected to the vacuum line and the solution was degased twice at -196°C by the usual freeze-thaw method. Carbon monoxide (7 mmole; 95 atom% ^{13}C -enriched) was then introduced into the reaction vessel at -196°C from the supply vessel and after thermal equilibration the reaction mixture was irradiated for 8 h.* Following the irradiation, the ^{13}CO gas of reduced enrichment was transferred to reaction vessel #2 which contained a further 300 mg (approximately) of $\text{BzCr}(\text{CO})_3$, while a fresh supply of 95 atom% ^{13}CO was introduced into reaction vessel #1. Both vessels were then irradiated for 8 h and the above procedure was repeated until all the steps shown in Table 1 had been completed. Since the final percent enrichment in each reaction vessel was not the same, the $\text{BzCr}(^{13}\text{CO})_3$ formed was recovered from each vessel separately by the following procedure. The contents of each reaction vessel were transferred into a 250-mL round-bottomed flask and the tetrahydrofuran solvent was evaporated off at room temperature on a rotary evaporator. Some $\text{Cr}(\text{CO})_6$ which had formed during the irradiations was removed by high-vacuum sublimation (0.01 torr/ 25°C) of the residues. The $\text{BzCr}(^{13}\text{CO})_3$ was recrystallized from diethyl ether/hexanes mixtures yielding a yellow, crystalline solid [0.83 g, 53% yield based on unlabelled $\text{BzCr}(\text{CO})_3$; mp $164\text{--}165^\circ\text{C}$; $\nu(\text{CO})$ (in CS_2) 1931.4s (\underline{a}_1), 1860.5s (\underline{e})]. Table 2 summarizes the results obtained for each reaction vessel.

Preparation of $\text{BzCr}(^{13}\text{CO})_2(\text{CX})$ ($\text{X} = \text{S}, \text{Se}$). These complexes were prepared from $\text{BzCr}(^{13}\text{CO})_3$ by the literature methods.^{5,6} The optimum reaction conditions were established during trial runs using unlabelled $\text{BzCr}(\text{CO})_3$.

*Prior to the preparative-scale reaction, the time necessary for statistical equilibration to occur was determined by irradiating small amounts of $\text{BzCr}(\text{CO})_3$ dissolved in tetrahydrofuran (2 mL) with a 5 molar excess of ^{13}CO . The exchange reactions were monitored by observing changes in the $\nu(\text{CO})$ region ($2000\text{--}1800\text{ cm}^{-1}$) of the infrared spectrum of the reaction mixture. Since no further changes occurred in this region after 8 h irradiation, it was assumed that a statistical distribution of ^{13}CO had been established.

Table 2. Reaction Yields for Each Vessel

Vessel	Irradiation time (h)	Wt BzCr(CO) ₃ added to vessel (g)	Wt residue (g)	BzCr(¹³ CO) ₃ % yield and (% of residue)	Cr(CO) ₆ % of residue
1	24	0.3084	0.1536	42% (85%)	14%
2	32	0.3041	0.2450	61% (77%)	22%
3	40	0.3121	0.2566	53% (66%)	33%
4	48	0.3120	0.2561	52% (64%)	32%
5	48	0.3137	0.2504	57% (72%)	27%

Cis-cyclooctene (20 mL)* and BzCr(¹³CO)₃ (350 mg) were added to 300 mL of benzene and the solution was irradiated for 50 min. The ultraviolet lamp was turned off and 25 mL of CS₂ (or 1.5 g of CSe₂) was added to the reaction mixture. After allowing the mixture to stand at 50°C for 2 h, the benzene solvent and excess C₈H₁₄ were removed on a rotary evaporator attached to a mechanical vacuum pump. The residue remaining contained the desired BzCr(¹³CO)₂(CX) complex mixed with about 10% BzCr(¹³CO)₃. These complexes were isolated by preparative thin layer chromatography, following the same procedures described in the literature^{5,6} for the unlabelled complexes. The thiocarbonyl and selenocarbonyl products were further purified by recrystallization from diethyl ether/hexanes mixtures: BzCr(¹³CO)₂(CS) [200 mg, 53% yield; mp 123°C (dec.); ν(CO) (in CS₂) 1923.7s (a'), 1880.0s (a'')]; BzCr(¹³CO)₂(CSe) [150 mg, 33% yield; mp 99 C (dec.); ν(CO) (in CS₂) 1930.2s (a'), 1887.9s (a'')].

RESULTS AND DISCUSSION

The results given in Table 2 for the exchange reaction of BzCr(CO)₃ with ¹³C clearly show that there is a competing reaction occurring, *viz.*, ¹³C substitution of the benzene ring to form ¹³C-labelled Cr(CO)₆. Although this

*A greater excess of C₈H₁₄ was used here compared to the literature because the reaction yields for these smaller-scale reactions were found to be improved under these conditions.

arene substitution reaction is slower than CO exchange, the long irradiation time necessary for the multistep enrichment allowed a considerable quantity of labelled $\text{Cr}(\text{CO})_6$ to be formed. In a previous study on the photochemical behaviour of $\text{BzCr}(\text{CO})_3$ in the presence of CO, no $\text{Cr}(\text{CO})_6$ was detected but the irradiation time was only 1 h.⁹ However, despite the build-up of labelled $\text{Cr}(\text{CO})_6$, the multistep exchange procedure reported here still yields a much greater quantity of highly-enriched $\text{BzCr}(\text{CO})_3$ per liter of ^{13}CO than would be expected from a single-step exchange.

The percent ^{13}C -enrichment of the $\text{BzCr}(^{13}\text{CO})_3$ produced was determined by infrared spectroscopy in the following manner. The absolute integrated intensity, A , of a fundamental infrared absorption band is proportional to the square of the partial derivative of the dipole moment with respect to the normal coordinate, $(\partial\mu/\partial Q)^2$. (However, if the normal coordinate and symmetry coordinate are identical, A becomes proportional to $(\partial\mu/\partial r)^2$ where r is a valence coordinate.¹⁰ Therefore, if equal concentrations and equal pathlengths are employed, the ratio of the absolute intensities of the labelled (A_{13}) and unlabelled (A_{12}) $\text{BzCr}(\text{CO})_3$ species is given by:

$$\frac{A_{13}}{A_{12}} = \frac{(\partial\mu/\partial r)_{13}^2}{(\partial\mu/\partial r)_{12}^2}$$

and if we further assume that the dipole moment derivative is constant, $A_{13} = A_{12}$. The absolute integrated intensities of the \underline{a}_1 CO stretching modes of $\text{BzCr}(^{12}\text{CO})_3$ and $\text{BzCr}(^{13}\text{CO})_3$ in hexanes solution were measured and the ratio, $A_{13}/A_{12} = 0.804$. This indicates that the labelled sample isolated contains 80.4% of the fully ^{13}C -labelled species and the percent ^{13}C -enrichment is therefore $(\sqrt[3]{0.804} \times 100) = 93\%$ which is in good agreement with the predicted value of 90%. The ^{13}C -enrichments of the $\text{BzCr}(^{13}\text{CO})_2(\text{CX})$ derivatives are similarly expected to be about 90%.

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