*Journal of Organometallic Chemistry*, 241 (1983) 45–51
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

# SYNTHESIS OF ARYLRHENIUM DERIVATIVES USING ORGANOCOPPER REAGENTS

JAMES R. SWEET and WILLIAM A.G. GRAHAM *

*Department of Chemistry, University of Alberta, Edmonton, Alberta T6G 2G2 (Canada)*

(Received July 6th, 1982)

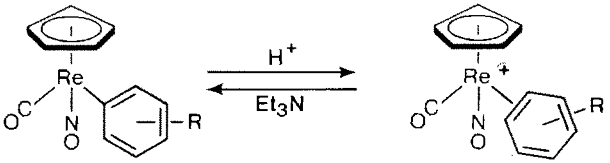
## Summary

Aryl derivatives ($\eta$-$C_5H_5$)Re(NO)(CO)R (R = $C_6H_5$, *o*-, *m*-, or *p*-tolyl, *m*- or *p*-trifluoromethylphenyl) have been conveniently prepared in 80–92% yields from ($\eta$-$C_5H_5$)Re(NO)(CO)Cl using an excess of the arylcopper reagents RCu. Reactions of ($\eta$-$C_5H_5$)Re(NO)(CO)X (X = Cl, Br, I) with phenylmagnesium bromide or phenyllithium afford the phenylrhenium compound in low yield or not at all, and an explanation is offered for this. Optimum reaction conditions, sources of the arylcopper reagent, and other variables in the syntheses have been explored.

---

## Introduction

In connection with our study of the interconversion of $\eta^1$-aryl and $\eta^2$-arene complexes of the ($\eta$-$C_5H_5$)Re(NO)(CO) group represented by eq. 1 [1,2], we required efficient and convenient methods for synthesis of *ortho*, *meta*, and *para* isomers of ($\eta$-$C_5H_5$)Re(NO)(CO)($\eta^1$-$C_6H_4$R) (R = $CH_3$, $CF_3$) as well as the phenyl derivative. The usual route to aryl compounds of metal carbonyls involves reaction of the appropriate carbonylmetalate anion with a substituted benzoyl halide, followed by decarbonylation [3]. However, the anion required in this case, [($\eta$-$C_5H_5$)Re(NO)(CO)]$^-$, has not yet been prepared [4] and appears to be unavailable by normally applicable reactions.



(1)

As an alternative, we have examined reactions that might substitute an aryl group for halide in ($\eta$-$C_5H_5$)Re(NO)(CO)X (X = Cl, Br, I). Although such attempts using Grignard or organolithium reagents were unsatisfactory, we have discovered that organocopper reagents function superbly to effect the desired substitution.

0022-328X/83/0000-0000/$03.00 © 1983 Elsevier Sequoia S.A.

## Results and discussion

Preliminary experiments on the reaction of aryl Grignard reagents with ($\eta$-$C_5H_5$)Re(NO)(CO)I established that the arylrhenium compounds were stable as expected, but yields were on the order of only 20%. Reasons for the poor yield in this and related reactions will be discussed later. An improved synthesis was sought because of the number of different arylrhenium compounds required as mentioned in the Introduction, and because the starting halides ($\eta$-$C_5H_5$)Re(NO)(CO)X (X = Cl, Br, I) were themselves obtained in a five step synthesis from $Re_2(CO)_{10}$.

It had been reported in 1956 by Piper and Wilkinson [5] that reaction of ($\eta$-$C_5H_5$)$Fe(CO)_2I$ with PhMgBr afforded only a 3–5% yield of ($\eta$-$C_5H_5$)$Fe(CO)_2(C_6H_5)$. We were therefore intrigued by a more recent report of Zakharkin et al. [6] that ($\eta$-$C_5H_5$)$Fe(CO)_2Br$ was converted to the phenyl derivative in 55% yield when the Grignard was first reacted with copper(I) chloride to form the organocopper reagent. As a result of this report, and the formal analogy to the established coupling reaction of RCu with alkyl halides [7], we decided to investigate this reaction with the rhenium halides.

### *Reactions of RCu with ($\eta$-$C_5H_5$)Re(NO)(CO)X*

The arylcopper reagents were prepared by dropwise addition of one mole of RMgX or RLi to an excess of copper(I) halide in THF or diethyl ether at 0°C. The reagent is thus an arylcopper, RCu, and not the more reactive organocuprate $[R_2Cu]^-$, which would require two mol of RMgX or RLi per mol of CuX. Recommended methodology for organic coupling reactions [7] is to use the arylcopper in preference to the organocuprate if the reaction proceeds at a tolerable rate, and that is certainly the case here.

Our initial experiments showed that yields of the arylrhenium complexes were much increased when arylcopper reagents were used, and detailed studies to optimize the conversion of ($\eta$-$C_5H_5$)Re(NO)(CO)X to its phenyl derivative established the following facts.

(1) Excess arylcopper reagent and longer reaction times are not harmful to the product and only increase the yield. Our starting point was a 2.5/1.0 molar ratio of arylcopper to rhenium halide, the minimum ratio recommended for organic substrates [7]. This ratio was increased to 5/1 for the tolylcopper reagents, which appear to decompose more rapidly.

(2) A Grignard reagent is preferred to phenyllithium for preparation of phenylcopper. For reasons as yet unknown, the lithium route in ether led to small quantities of an unidentified product containing the ($\eta$-$C_5H_5$)Re(NO)(CO) group, complicating the workup.

(3) Variation of X in ($\eta$-$C_5H_5$)Re(NO)(CO)X established that the yield increased in the order $I^- < Br^- < Cl^-$. This is contrary to expectations based on leaving group behavior, and suggests that the reaction is facilitated by increased polarity of the $Re^{\delta+}$–$X^{\delta-}$ bond. The trend in yields probably reflects the rate of reaction with substrate since the arylcopper reagents are themselves unstable.

(4) Recovery of pure product is greatly simplified when the initial rhenium halide is essentially completely consumed.

Thus, in the optimized synthesis of ($\eta$-$C_5H_5$)Re(NO)(CO)$C_6H_5$, ($\eta$-$C_5H_5$)Re(NO)(CO)Cl (1 mol) was added at 0°C to a THF suspension of phenylcopper (formed from 2.5 mol of PhMgBr and 5.0 mol CuBr) and the reaction continued at room temperature for 1 h. IR monitoring showed that the rhenium halide had been entirely consumed. Hydrolysis with a small excess of water and a single recrystallization afforded the analytically pure product in 91% yield.

### *Properties of the arylrhenium compounds*

The products are thermally very robust, as expected from the high stability of other ($\eta$-$C_5H_5$)Re(NO)(CO) derivatives such as hydride [4] and $\eta^1$-cycloheptatrienyl [8]. Substituent effects upon carbonyl and nitrosyl stretching frequencies are not large (Table 1), but in the trifluoromethyl derivatives shifts of 6–8 $cm^{-1}$ to higher frequency are noted. This reasonable trend is paralleled by small changes in the $\eta$-$C_5H_5$ $^1H$ NMR resonances, ca. 0.03 ppm upfield in the tolyl derivatives and ca. 0.03 ppm downfield in the trifluoromethyl compounds.

It was important in our studies of the deprotonation of arene cations (eq. 1) to be able to distinguish the isomeric aryl derivatives spectroscopically. A careful study was therefore made of the aromatic region of the $^1H$ NMR spectra of these compounds, as indicated in Table 2 and Fig. 1. At 400 MHz, the spectra are approximately first order. *Ortho* proton–proton couplings are ca. 7.5 Hz, *meta* couplings about 1.5 Hz, and *para* couplings $< 0.5$ Hz (observable only as a slight broadening).

A partial assignment can be made in spectra such as those in Fig. 1 from the singlet, doublet, and triplet patterns. The assignment can be completed by decou-

TABLE 1

COLORS, YIELDS, ANALYTICAL AND IR DATA FOR NEW COMPOUNDS

| R | Color | Yield (%) | Analyses (Found (calcd.) (%)) | | | IR [a] | |
|---|---|---|---|---|---|---|---|
| | | | C | H | N | $\nu(CO)$ $(cm^{-1})$ | $\nu(NO)$ $(cm^{-1})$ |
| $C_6H_5$ | orange | 91 | 37.23<br>(37.30) | 2.67<br>(2.61) | 3.58<br>(3.62) | 1981 | 1725 |
| $o$-$C_6H_4CH_3$ | orange-red | 80 | 38.83<br>(38.99) | 3.06<br>(3.02) | 3.44<br>(3.50) | 1980 | 1719 [b] |
| $m$-$C_6H_4CH_3$ | orange-red | 85 | 38.78<br>(38.99) | 2.98<br>(3.02) | 3.51<br>(3.50) | 1980 | 1724 |
| $p$-$C_6H_4CH_3$ | orange | 90 | 38.99<br>(38.99) | 3.02<br>(3.02) | 3.51<br>(3.50) | 1980 | 1724 |
| $m$-$C_6H_4CF_3$ | red | 89 | 34.58<br>(34.36) | 2.08<br>(2.00) | 3.01<br>(3.08) | 1988 | 1731 |
| $p$-$C_6H_4CF_3$ | orange | 92 | 34.37<br>(34.36) | 2.05<br>(2.00) | 3.04<br>(3.08) | 1987 | 1730 |
| Cl | dk red | 96 | 20.89<br>(20.90) | 1.42<br>(1.46) | 4.03<br>(4.06) | 2001 | 1740 |
| I [c] | dk red | 94 | 16.49<br>(16.52) | 1.12<br>(1.16) | 3.15<br>(3.21) | 2003 | 1746 |

[a] In hexane solution. [b] Prominent shoulder on high frequency side attributed to rotamer effects. [c] Data for this compound have been reported in a different solvent [14].

TABLE 2

$^1$H NMR DATA FOR ($\eta$-$C_5H_5$)Re(NO)(CO)R DERIVATIVES [a]

| R | δ(ppm) | | | | | | |
|---|---|---|---|---|---|---|---|
| | $C_5H_5$ | $CH_3$ | H(2) | H(3) | H(4) | H(5) | H(6) |
| $C_6H_5$ | 5.69s | - | 7.50m | 7.02m | 7.02m | 7.02m | 7.50m |
| $o$-$C_6H_4CH_3$ | 5.662s | 2.40s | - | 7.52d | 6.78t | 6.91t | 7.09d |
| $m$-$C_6H_4CH_3$ | 5.665s | 2.22s | 7.33s | - | 7.26d | 6.89t | 6.77d |
| $p$-$C_6H_4CH_3$ | 5.668s | 2.27s | 6.87d | 7.37d | - | 7.37d | 6.87d |
| $m$-$C_6H_4CF_3$ | 5.72s | - | 7.72s | - | 7.68d | 7.12t | 7.21d |
| $p$-$C_6H_4CF_3$ | 5.72s | - | 7.22d | 7.60d | - | 7.60d | 7.22d |

[a] $^1$H NMR spectra at 400 MHz in $CD_2Cl_2$; s = singlet, d = doublet, t = triplet, m = multiplet. Numbering system for substituted phenyl derivatives is shown in Fig. 1.

pling and NOE experiments (irradiation of the methyl protons), which establish that the resonances of aromatic protons *ortho* to the transition metal are shifted to lower field. We have noted the same trend previously in other aryl complexes of the rhenium group [2].

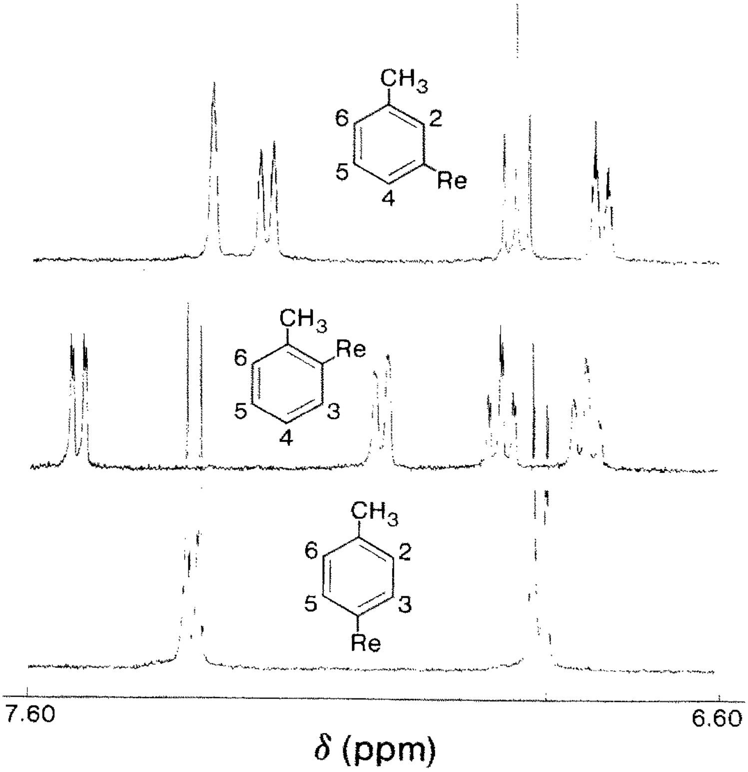


Fig. 1. Proton NMR spectra (400 MHz, $CD_2Cl_2$) of tolyl derivatives of the ($\eta$-$C_5H_5$)Re(NO)(CO) group: Upper spectrum, *meta* isomer; middle spectrum, *ortho* isomer; lower spectrum, *para* isomer. Numbering system shown is used in Table 2, where assignments and exact chemical shifts are presented.

*Problems with aryllithium and Grignard reactions*

As noted above, reaction of PhMgBr with ($\eta$-$C_5H_5$)Re(NO)(CO)I led to the phenylrhenium product in only about 20% yield. Infrared spectra (bands at 1645 and 1490 $cm^{-1}$) of reaction mixtures indicated formation in a parallel reaction of fairly large amounts of a product we formulate as $[(\eta\text{-}C_5H_5)Re(NO)\{C(O)Ph\}I]^-$. This would result from carbanion attack on the carbonyl group without subsequent loss of iodide. The proportion of benzoylmetalate product was greater for the rhenium bromide and still greater for the chloride, consistent with increasing positive charge on the carbonyl carbon. In the reaction of phenyllithium with all three rhenium halides, the corresponding metalates appear to be the exclusive products, as judged by IR. We did not attempt to isolate these anionic products.

There are precedents for formation of related acylmetalate species in the reaction of metal carbonyl halides with lithium carbanions, all involving rhenium as it happens [9,10,11]. In the most relevant case, the anion $[Ph_3P(OC)_3Re(COCH_3)Br]^-Li^+$ was isolated from the reaction of $Ph_3P(OC)_4ReBr$ with $CH_3Li$; it was proposed that the anion lost LiBr in THF at 50°C forming $Ph_3P(OC)_4ReCH_3$ [11]. We did not observe the conversion of the benzoylmetalate anions presumed to form in our system to the desired aryl products, even when solutions were heated or $AgBF_4$ was added in an attempt to promote the reaction by abstracting halide ion.

In the Introduction we referred to the low yields (3–5%) obtained in the reaction of PhMgBr with ($\eta$-$C_5H_5$)Fe$(CO)_2$I [5]. A similar problem, attack of carbonyl carbon to form an acylate anion which does not readily lose halide, is probably involved. It is interesting to note that conversion of the phosphine-substituted iodide ($\eta$-$C_5H_5$)Fe(CO)($PPh_3$)I to the corresponding primary alkyls using alkyllithium reagents proceeds in yields of 50–60% [12]. The suggestion has been made that initial attack of the carbonyl carbon takes place in this reaction [13]. If that is the case, destabilization of the acylate ion by the phosphine ligand would account for the improved yield. However, it may be that the reduced positive charge on the carbonyl carbon (cf. the reduced carbonyl stretching frequency) resulting from the phosphine ligand completely suppresses the acylate anion pathway.

Whatever the mechanism of the arylcopper reaction, it may be presumed not to involve nucleophilic attack on the substrate. Thus, what appears to be the source of the difficulty with carbanionic reagents is avoided.

## Conclusion

Aryl derivatives ($\eta$-$C_5H_5$)Re(NO)(CO)R can be prepared conveniently and in high yield by reaction of ($\eta$-$C_5H_5$)Re(NO)(CO)Cl with arylcopper reagents derived from Grignard reagents. We intend to explore the value of arylcopper reagents in similar coupling reactions with other transition metal halide substrates, as well as the potential of alkylcopper reagents. The process of metal–carbon bond formation from metal carbonyl halides is of fundamental importance in organometallic chemistry. It may be that organocopper reagents will be of general value in overcoming difficulties which arise when carbanionic reagents are used.

## Experimental

*General procedures*

Reactions were carried out under a nitrogen atmosphere using solvents dried by standard procedures and distilled just prior to use. Glassware was oven dried and cooled under a nitrogen stream.

Dirhenium decacarbonyl (Strem Chemicals, Inc.), phenyllithium (Aldrich), phenylmagnesium bromide (2.3 *M* in THF, Alfa), and copper(I)bromide (Aldrich) were used as received. Other Grignard reagents were prepared at approximately 1 *M* by stirring 10 mmol of the appropriate bromide (Aldrich) with 11 mmol of magnesium in THF (10 ml) for 2 h at room temperature.

Analyses were performed by the Microanalytical Laboratory of this Department. IR spectra were measured using a Nicolet MX-1 FT instrument. Mass spectra were obtained by use of an A.E.I. MS-12 spectrometer with Kratos D550 data acquisition system; source temperatures varied from 50 to 90°C and ionizing voltages of 14–16 eV were found to produce a simplified pattern. In every case, the principal fragments were $M^+$, $(M - CO)^+$, and $(M - CO - NO)^+$. NMR spectra were recorded using a Bruker WH-400 FT spectrometer.

Yields, colors, microanalytical results, and infrared data for all new compounds are given in Table 1. $^1$H NMR data are collected in Table 2 and spectra of the tolyl derivatives are shown in Fig. 1.

### Preparation of $(\eta\text{-}C_5H_5)Re(NO)(CO)C_6H_5$

A solution of phenylmagnesium bromide (0.63 ml, 1.45 mmol) was added dropwise to a stirred suspension of CuBr (0.42 g, 2.90 mmol) in 10 ml THF cooled to 0°C. Solid $(\eta\text{-}C_5H_5)Re(NO)(CO)Cl$ (0.20 g, 0.58 mmol) was introduced in one batch and the vessel allowed to warm to room temperature as stirring continued. After 1 h the dark red suspension was hydrolyzed with water (0.20 ml, 11.1 mmol) and filtered through a "D" porosity frit packed with filter aid (Celite). Solvent was removed from the filtrate under reduced pressure and after overnight drying under vacuum the solid residue was extracted with hexane (3 × 10 ml). The combined extracts were filtered and solvent was removed at reduced pressure to give a pale reddish powder. Recrystallization from the minimum volume of hexane by slow cooling to −78°C afforded the product as bright orange crystals (0.22 g, 91%).

### Preparation of o-, m-, and p-tolyl derivatives

The procedure above was followed except that 2.90 mmol of the appropriate tolylmagnesium bromide and 5.80 mmol of CuBr in 20 ml THF were used for reaction with 0.58 mmol of $(\eta\text{-}C_5H_5)Re(NO)(CO)Cl$, and stirring was continued for 3 h before hydrolysis.

### Preparation of m- and p-trifluoromethylphenyl derivatives

The above procedure was followed except that 2.90 mmol of the appropriate Grignard and 5.80 mmole CuBr were used in 20 ml THF for reaction over 2 h with 1.16 mmol $(\eta\text{-}C_5H_5)Re(NO)(CO)Cl$.

### Preparation of $(\eta\text{-}C_5H_5)Re(NO)(CO)X$ ($X = Cl, I$)

These halides were prepared in yields of 96 and 94%, respectively by reaction of $(\eta\text{-}C_5H_5)Re(NO)(CO)H$ with *N*-chloro- and *N*-iodo-succinimide under the same conditions previously reported for preparation of the bromide [4]. $^1$H NMR ($CD_2Cl_2$): X = Cl, δ 5.86 ($C_5H_5$); X = I, δ 5.87 ($C_5H_5$). IR: see Table 1.

## Acknowledgement

We thank the Natural Sciences and Engineering Research Council of Canada and the University of Alberta for financial support.

## References

1 J.R. Sweet and W.A.G. Graham, to be published.
2 J.R. Sweet and W.A.G. Graham, Organometallics, in press.
3 R.P. Stewart and P.M. Treichel, J. Am. Chem. Soc., 92 (1970) 2710.
4 J.R. Sweet and W.A.G. Graham, Organometallics, 1 (1982) 982.
5 T.S. Piper and G. Wilkinson, J. Inorg. Nucl. Chem., 3 (1956) 104.
6 L.I. Zakharkin, A.I. Kovredov, M.G. Meiramov and A.V. Kazantsev, Izvest. Akad. Nauk SSSR, Ser. Khim., (Eng. Transl.), (1977) 1544.
7 G.H. Posner, Organic Reactions, 22 (1975) 253.
8 J.R. Sweet and W.A.G. Graham, J. Organometal. Chem., 217 (1981) C37.
9 K.P. Darst and C.M. Lukehart, J. Organometal. Chem., 171 (1979) 65.
10 K.P. Darst, P.G. Lenhert, C.M. Lukehart and L.T. Warfield, J. Organometal. Chem., 195 (1980) 317.
11 D.W. Parker, M. Marsi and J.A. Gladysz, J. Organometal. Chem., 194 (1980) C1.
12 D.L. Reger and E.C. Culbertson, Syn. React. Inorg. Metal-Org. Chem., 6 (1976) 1.
13 D.H. Gibson, W.-L. Hsu and F.U. Ahmed, J. Organometal. Chem., 215 (1981) 379.
14 B.W. Hames, B.W.S. Kolthammer and P. Legzdins, Inorg. Chem., 20 (1981) 650.