nism of these reactions. Since no quantitative oxidative cleavage of dppm or dpam ligands occurs when **1a** or **1b** are heated at 80–85 °C for 90 min, the oxidative addition of hydrogen has likely preceded the oxidative cleavage of the ligand. Is there any possibility to obtain activation of hydrogen without oxidative cleavage of dppm or dpam ligands? Such a reaction has not been observed until now. The oxidative addition of hydrogen seems to promote subsequent cleavage of these ligands; it also provides a satisfactory control of these reactions which do not go further: both complexes **3a** and **3b** were recovered unchanged after prolonged reflux in dibutyl ether (145 °C).

Preliminary Catalytic Runs. The hydrogenation of cyclohexanone was chosen as a first test, owing to the known efficiency of $H_4Ru_4(CO)_{12}$ and related phosphine derivatives for this reaction.[7] The preliminary results mentioned here were obtained under experimental conditions close to those stated in the referenced paper:[7] no attempt was made to check the influence of temperature and hydrogen pressure on the rate of the hydrogenation reaction. Although attempts to use **1a** as the loaded form of the catalyst gave poor conversion yields, direct use of the dihydride species **3a** led to satisfactory results. It should be noted that the rate of hydrogenation is lower than that obtained for $H_4Ru_4(CO)_{12}$. Nevertheless, the amount of 89.8% conversion after 18 h is close to the best results obtained by using phosphine-substituted derivatives of $H_4Ru_4(CO)_{12}$ under closely related experimental conditions.[7] The important point, however, is that a degradation of the cluster frame of **3a** is avoided under the reported conditions. Indeed, after the hydrogenation reaction, the cluster **3a** could be recovered unchanged. This result supports previous design of nonfluxional face-bridging ligands in view of cluster catalysis,[3,8] despite the known limited use of such complexes under extremely severe conditions.[40] Following the previous demonstrations that a reversible opening of metal–metal bonds may have a role in cluster catalysis,[41–44] we would suggest that the activity of **3a** could be related to the observed mobility of the hydride ligand providing active sites through a reversible opening of M–H–M bonds.

We are now exploring possible new applications of these complexes in catalysis. Some of these applications may be inferred from our recent observation[45] that the dihydrido cluster complexes can be synthetized through the reaction of **1a** or **1b** with water. We emphasize that investigators in catalysis with phosphine-substituted clusters should be aware of possible transformations of such complexes under catalytic conditions. Let us recall an earlier communication[2] concerning a hydroformylation of propene using $Rh_4(CO)_{10}(PPh_3)_2$ for which a catalytic reaction was observed together with decomposition of the phosphine.

Acknowledgment. Financial assistance from CNRS (ATP "Chimie Fine") and DGRST is gratefully acknowledged.

Registry No. 1a, 77611-27-9; **1b,** 81875-88-9; **2b,** 81875-89-0; **3a,** 81875-90-3; **3b,** 81875-91-4; cyclohexanone, 108-94-1.

Supplementary Material Available: Table III, Table V, Table VI, and a listing of structure factor amplitudes for compounds **3a** and **3b** (47 pages). Ordering information is given on any current masthead page.

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(41) Keister, J. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1976,** *18,* 1056.

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(44) Ford, P. C. *Acc. Chem. Res.* **1981,** *14* (2), 31.

(45) Lavigne, G.; Brisson, C.; Bonnet, J.-J., unpublished results.

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^{13}C DNMR Study of $[(Ph_3P)_2N][CoRu_3(CO)_{13}]$. Evidence for a Unique Fluxional Process Which Involves Concerted Motion of 12 Carbonyl Ligands and Leads to Rapid Interconversion of Enantiomers

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Received April 7, 1982

A variable-temperature ^{13}C NMR study has been conducted on $[(Ph_3P)_2N][CoRu_3(CO)_{13}]$, a tetranuclear cluster with a chiral arrangement of carbonyl ligands. The spectral data indicate that the lowest energy exchange process involves concerted motion of 12 of the 13 carbonyls and leads to interconversion of the two enantiomers of the cluster anion.

The cluster anion $[CoRu_3(CO)_{13}]^-$ has been shown by an X-ray diffraction study to adopt the unique structure shown in Figure 1 with carbonyls bridging each of the three Co–Ru bonds.[1,2] These bridging carbonyls are positioned such that each is nearly coplanar with one of the three $CoRu_2$ faces. Furthermore, as shown in Figure 2, the three terminal carbonyls on each Ru are nonequivalent. This

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(1) Steinhardt, P. C.; Gladfelter, W. L.; Harley, A. D.; Fox, J. R.; Geoffroy, G. L. *Inorg. Chem.* **1980,** *19,* 332.

(2) The only other cluster known to have a distribution of CO ligands similar to that in $[CoRu_3(CO)_{13}]^-$ is $[FeRu_3(CO)_{12}(NO)]^-$: Fjare, D. E.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1981,** *103,* 1572.

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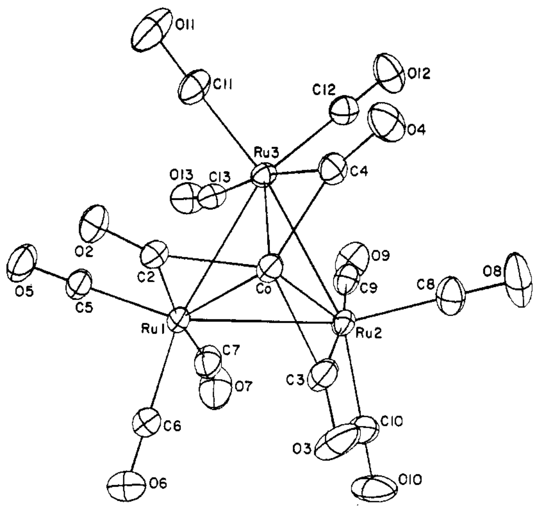


Figure 1. An ORTEP drawing of the $[CoRu_3(CO)_{13}]^-$ anion taken from ref 1. Thermal ellipsoids are drawn at the 20% probability level. The terminal carbonyl (C_1O_1) attached to Co is omitted for clarity.

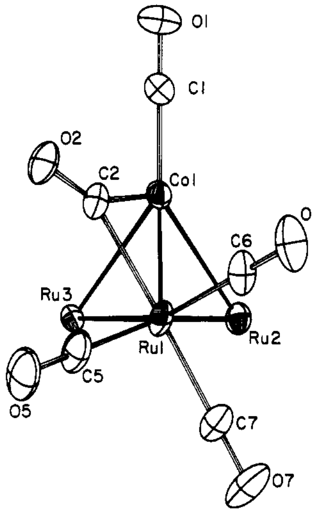
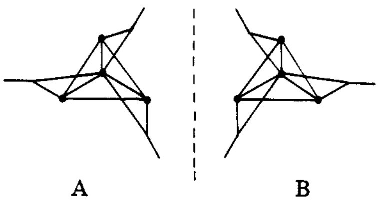


Figure 2. An ORTEP drawing of a portion of the $[CoRu_3(CO)_{13}]^-$ anion which illustrates the nonequivalence of the terminal carbonyls on Ru_1.

particular arrangement of carbonyl ligands renders the $[CoRu_3(CO)_{13}]^-$ cluster chiral with an overall symmetry of C_3. This is best illustrated by the diagrams below which show the metal framework and the disposition of the three bridging CO's. The enantiomer on the left, A, is clearly not superimposable on its mirror image, B.



The cluster crystallizes in the centrosymmetric space group $P\bar{1}$, and thus both enantiomers are present in the unit cell.[1] This raises the interesting possibility of a low-energy racemization pathway for the cluster anion, and accordingly a variable-temperature ^{13}C NMR study was undertaken. As detailed herein, evidence has been obtained for a unique fluxional process which leads to rapid interconversion of the two enantiomers and involves a simultaneous movement of 12 of the 13 carbonyl ligands.

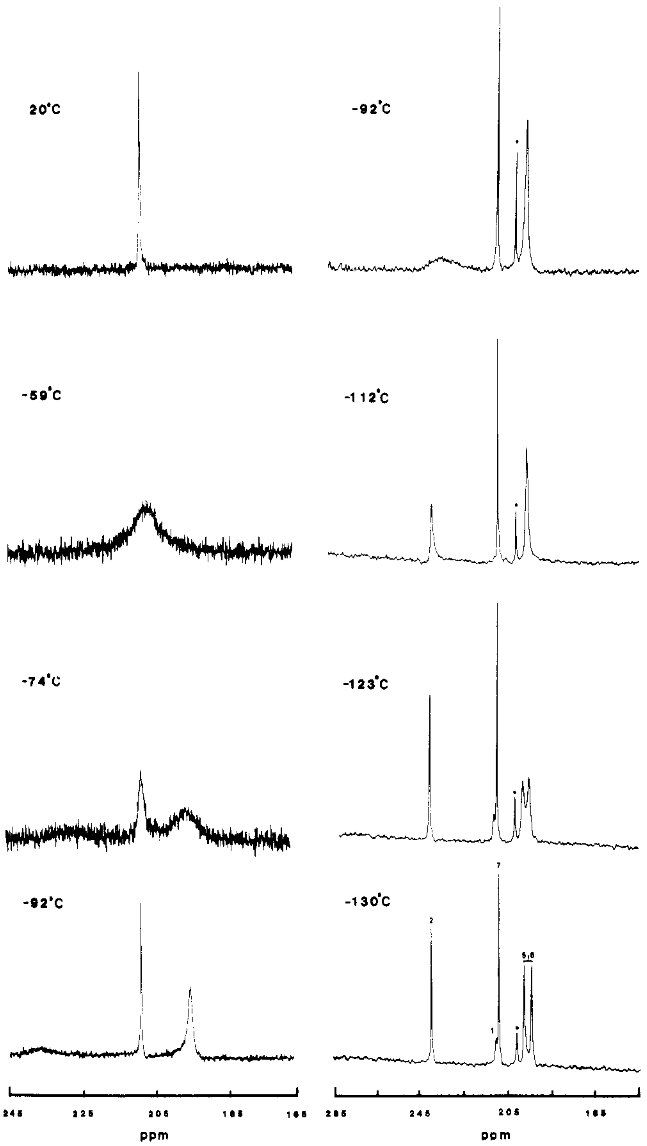


Figure 3. Variable-temperature ^{13}C NMR spectra of $[(Ph_3P)_2N][CoRu_3(CO)_{13}]$. Only the CO region of the spectrum is shown. The spectra on the right (−130 → −92 °C) were recorded in a 9:1 $CHFCl_2/CD_3OD$ solvent mixture. The resonance marked with the asterisk is due to $Ru_3(CO)_{12}$ impurity. The spectra on the left (−92 → 20 °C) were recorded in a 9:1 CH_2Cl_2/CD_3OD solvent mixture.

Experimental Section

$[(Ph_3P)_2N][CoRu_3(CO)_{13}]$ was prepared according to the literature procedure.[1] Since the cluster anion readily fragments when placed under a CO atmosphere,[3] enrichment was carried out by synthesizing the cluster with ^{13}CO enriched $Ru_3(CO)_{12}$. A final enrichment of ~20% was obtained. ^{13}C NMR spectra were obtained on a Brüker WH 400-MHz NMR spectrometer at the University of South Carolina in the National Science Foundation's Regional NMR Facility. $Cr(acac)_3$ (~0.001 M) was added to each sample as a "shiftless relaxation agent",[4] and the concentration of $[(Ph_3P)_2N][CoRu_3(CO)_{13}]$ was 6×10^{-4} M. All spectra were referenced to external Me_4Si. Each spectrum was recorded with an acquisition time of 0.13 s, a digital resolution of 7.6 Hz/point, and 744 accumulations/spectrum. The probe temperature was determined by using a calibrated thermocouple and is accurate to ±1 °C.

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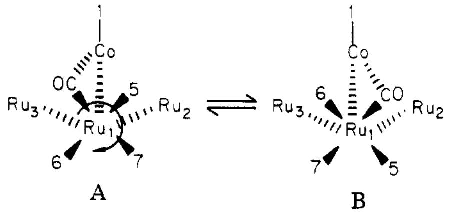
(3) Fox, J. R.; Gladfelter, W. L.; Geoffroy, G. L. *Inorg. Chem.* **1980**, *19*, 2574.

(4) Gansow, O. A.; Burke, A. R.; LaMar, G. N. *J. Chem. Soc., Chem. Commun.* **1972**, 456.

Results and Discussion

The results of the variable-temperature ^{13}C NMR study of $[CoRu_3(CO)_{13}]^-$ are shown in Figure 3. The 20 °C spectrum shows a single broad resonance at 209.1 ppm, implying rapid exchange of all 13 carbonyl ligands at this temperature. Five resonances were resolved upon cooling to −130 °C, and these correspond to the five nonequivalent carbonyl ligands shown in the solid-state structure. The labeling scheme used in the spectral assignment corresponds to that of Figure 2. The singlet at 242.1 ppm of relative intensity 3 is assigned to the three equivalent bridging carbonyl ligands 2 since bridging carbonyls generally appear further downfield than terminal carbonyls.[5] The 211.1-ppm singlet of relative intensity 1 is logically attributed to the terminal carbonyl on cobalt, 1. The remaining three singlets at 209.7, 197.6, and 193.8 ppm, each of relative intensity 3, are assigned to the three sets of nonequivalent terminal carbonyl ligands on the ruthenium atoms, 5, 6, and 7. The present data do not allow these carbonyl ligands to be distinguished, but the variable-temperature data discussed below indicate that the two furthest upfield resonances are due to carbonyls 5 and 6.

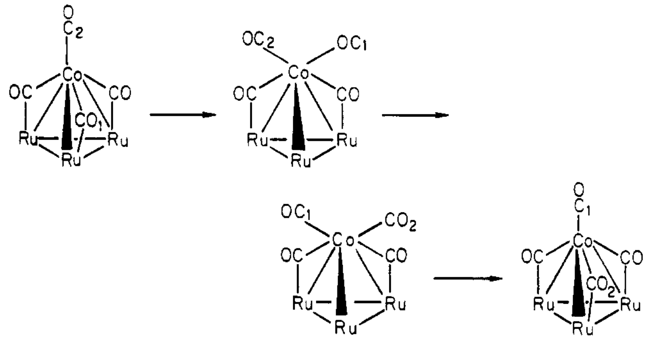
When the solution is warmed from −130 °C, the δ 197.6 and 193.8 resonances broaden and by −112 °C have coalesced into a single resonance at δ 195.7. Only these two resonances are affected in moving from −130 to −123 °C, implying that these two terminal carbonyls on Ru exchange with each other but not with the third Ru carbonyl nor with any other in this temperature range. We suggest that the δ 197.6 and 193.8 resonances are due to carbonyls 5 and 6 and that their exchange occurs by a process which interconverts the two enantiomers. Consider the diagrams shown in eq 1 which depict the stereochemistry about Ru.



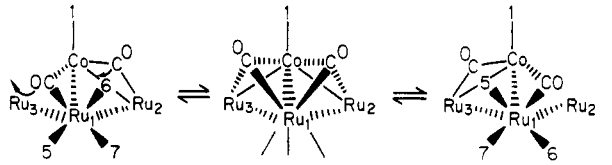
(1)

If the $Ru(CO)_4$ group were to rotate such that the bridging CO were to move from its initial position coplanar with the Ru_1Ru_2Co face, A, to a position coplanar with the Ru_1Ru_3Co face, B, carbonyls 5 and 6 would exchange environments. Although the bridging carbonyl and carbonyl 7 move during this process, their environment is the same in both A and B and their resonances are not affected. Of course, such an exchange process cannot be localized at one Ru and must involve a similar concerted movement at the other two Ru centers. In essence, 12 of the 13 carbonyls must move together in a concerted process with the one terminal carbonyl on Co not participating. The carbonyl movement changes the relative orientation of the bridging carbonyls and thus leads to interconversion of the two enantiomers. The key feature of this interpretation is that although the two enantiomers have identical ^{13}C NMR spectra, as they must, their interconversion is sensed by the diastereotopic carbonyls 5 and 6 which exchange environments during the racemization. This exchange has an estimated lifetime (τ) of 2.2 (±0.6) × 10^{-3} s at −123 °C,[6,7a] from which an activation free energy ($\Delta G^{\ddagger}$) of 28.2 ± 2.0 kJ/mol can be calculated for the racemization process.[6,7b,c]

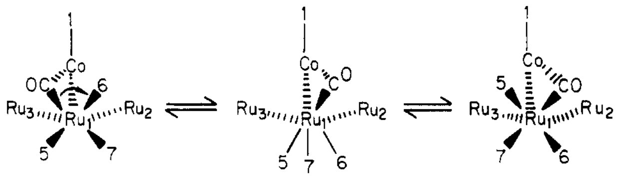
Scheme I



Scheme II



Scheme III



The −112 °C spectrum also shows the loss of the resonance assigned to the terminal carbonyl on cobalt and a broadening of the 242-ppm resonance due to the bridging CO's. This presumably reflects exchange between the terminal cobalt carbonyl and the three bridging ligands. Such exchange most likely occurs by the process shown in Scheme I which involves opening one of the carbonyl bridges, a subsequent twist of the resultant $Co(CO)_2$ unit, and finally reforming the CO bridge. Such an exchange process predicts that the resonance due to the terminal CO would broaden faster than that due to the bridging CO's since the former exchanges in every process whereas the latter only one in three.[8] This is indeed observed since at −112 °C the resonance due to carbonyl 1 has collapsed into the baseline whereas that due to 2 has only broadened. A similar bridge–terminal exchange process has been proposed for $H_2FeRu_3(CO)_{13}$, $H_2FeRu_2Os(CO)_{13}$, and $H_2FeRuOs_2(CO)_{13}$.[9]

Further warming leads to continued broadening of the bridging carbonyl resonance until at −74 °C only two broad singlets are observed due to the terminal carbonyls on

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[5] (a) Evans, J.; Johnson, B. F. G.; Lewis, J.; Norton, J. R.; Cotton, F. A. *J. Chem. Soc., Chem. Commun.* **1973**, 807. (b) Johnson, B. F. G.; Lewis, J.; Matheson, T. W. *Ibid.* **1974**, 441. (c) Stuntz, G. F.; Shapley, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 607. (d) Geoffroy, G. L.; Gladfelter, W. L. *Ibid.* **1977**, *99*, 6775.

[6] Martin, M. L.; Delpuech, J. J.; Martin, G. J. "Practical NMR Spectroscopy"; Heyden: Philadelphia, PA, 1980.

[7] (a) The lifetime for this exchange between two equally populated sites in which the line widths are small relative to the peak separation at −123 °C was calculated by using eq 8.14 on p 300 of ref 6. In our case $\Delta\nu_{max}$ = 374 Hz and r' = 1.88 ± 1. The uncertainty was estimated by a qualitative assessment of the uncertainty in the experimental data. (b) Calculated from eq 8.64 on p 340 of ref 6 using κ = 1 and $k = 1/\tau$. (c) A value of $\Delta G^{\ddagger}$ = 28.4 ± 2.0 kJ/mol was also calculated from the −112 °C spectrum (after coalescence) following the procedure given in Section 1.3.2 on page 299 of ref 6 with $\Delta\nu_{1/2}$ = 121 Hz.

[8] The observed differential broadening may be in part due to different degrees of temperature-dependent ^{59}Co quadrapolar broadening of the bridging and terminal Co carbonyl resonances. The extreme broadening observed does strongly argue for a fluxional process, although the experimental data do allow an accurate assessment to be made of the relative contributions of the fluxional process and the quadrapolar effect to the observed line broadening.

[9] Gladfelter, W. L.; Geoffroy, G. L. *Inorg. Chem.* **1980**, *19*, 2579.

ruthenium. The breadth of these singlets indicates that exchange is now occurring between the bridging CO's and the terminal CO's on Ru, most likely through a process similar to that of Scheme I. Further warming leads to total exchange of all carbonyls by a combination of these processes.

The racemization process is the crucial element of this study as it represents the concerted motion of at least 12 carbonyl ligands and it occurs with an exceedingly low activation energy. We know of no precedent for such a process. There appear to be two plausible mechanisms for this exchange which differ in subtle detail. These are illustrated in Schemes II and III. The exchange could proceed through an intermediate in which the three carbonyls become fully face bridging and then migrate to the other ruthenium atom in the face, Scheme II. The $Ru(CO)_3$ group would have to twist to accomodate this motion, and carbonyls 5 and 6 would exchange. The second mechanism, Scheme III, would involve a movement of the bridging carbonyls from their facial-coplanar arrangement to an edge-bridging position in which they lie in a plane perpendicular to that containing the opposite face of the cluster. From this C_{3v} intermediate the other enantiomer can be obtained by movement of this carbonyl to a facial-coplanar arrangement with the adjacent face of the cluster. This of course requires movement of the terminal Ru carbonyls and results in exchange of carbonyls 5 and 6. This is in essence the process depicted in eq 1. Although the present data do not allow a distinction between these two possible mechanisms, the second seems more likely for a concerted path involving 12 carbonyl ligands since it involves a minimum amount of bond breaking and forming.

Acknowledgment. We thank the Department of Energy for support of this research and Dr. Charles DeBrosse for assistance with some of the early NMR experiments. We also acknowledge the assistance of personnel at the National Science Foundation's Regional NMR Facility at the University of South Carolina, Charleston, SC, operated under NSF Grant CHE 78-18723. G.L.G. gratefully acknowledges the Camille and Henry Dreyfus Foundation for a Teacher-Scholar Award (1978–1983).

Registry No. $[(Ph_3P)_2N][CoRu_3(CO)_{13}]$, 72152-11-5.

Addition of Grignard Reagents and Ketone Enolates to the Arene in (Arene)manganese Tricarbonyl Cations

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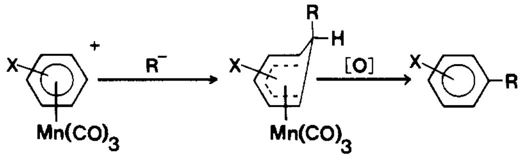
Grignard reagents and ketone enolates add to the arene ring in $[(arene)Mn(CO)_3]^+$ to give good yields of thermally stable cyclohexadienyl complexes which are easily oxidized with Jones reagent to give the functionalized arenes. A method to free the functionalized arene that allows isolation and recycling of the $Mn(CO)_3^+$ moiety is also described. Addition to substituted arenes is shown to be regioselective in a predictable manner. It seems that the (arene)manganese complexes will prove to be of significant utility in organic synthesis.

Introduction

Coordinated arenes and other cyclic π-hydrocarbons can be functionalized by nucleophile addition provided the hydrocarbon ring is sufficiently activated. The cyclohexadienyl ring[1] in $[(C_6H_7)Fe(CO)_3]^+$ and the arene ring[2] in $[(arene)Cr(CO)_3]$ have been extensively investigated in this regard. The $[(arene)Cr(CO)_3]$ complexes are readily synthesized with a variety of arenes, and the ring is electrophilic enough to react with strong nucleophiles such as organolithium reagents to give cyclohexadienyl complexes that can be oxidized to free the functionalized arene. The principal limitation with the $[(arene)Cr(CO)_3]$ complexes is the requirement that the nucleophile be very strong. Synthetically useful nucleophiles such as Grignard reagents and ketone enolates give little or no product.

The arene in $[(arene)Mn(CO)_3]^+$ (1) is known[3,4] to be far more electrophilic than in $[(arene)Cr(CO)_3]$, and so the manganese complexes are at least potentially more versatile synthetic reagents. Their use so far has been very limited due to solubility problems because of the positive charge and, more importantly, the rather severe conditions used for their synthesis, which limits the arenes that can be complexed without substituent isomerization or modification. Recently, however, very mild procedures have been reported[5] that allow the synthesis of $[(arene)Mn(CO)_3]^+$ with a wide variety of arenes.

It is known[6] that organolithium reagents add to the ring in $[(arene)Mn(CO)_3]^+$. In this paper we report that Grignard reagents and ketone enolates also add in high yield and that the resulting cyclohexadienyl complexes (2) are easily oxidized to give the functionalized arene as in reaction 1. A method to free the functionalized arene that



1 2 (1)

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[3] Walker, P. J. C.; Mawby, R. J. *Inorg. Chim. Acta* **1973**, *7*, 621.

[4] Kane-Maguire, L. A. P.; Sweigart, D. A. *Inorg. Chem.* **1979**, *18*, 700.

[5] Bhasin, K. K.; Balkeen, W. G.; Pauson, P. L. *J. Organomet. Chem.* **1981**, *204*, C25.

[6] Pauson, P. L.; Segal, J. A. *J. Chem. Soc., Dalton Trans.* **1975**, 1683.

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