The [Re(CO)₆]⁺ Cation as a Ligand-Transfer Reagent with Ferrocene Derivatives

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The $[\text{Re}(\text{CO})_6]^+$ cation is a stable compound, soluble in aqueous media. We show that it can be used as a reagent in the synthesis of tricarbonyl(cyclopentadienyl)rhenium complexes. $[\text{Re}(\text{CO})_6]^+$ reacts with ferrocene derivatives, particularly acetylferrocene, in DMSO, DMF or a water/DMSO (1:1) mixture at 160 $^{\circ}\mathrm{C}$ to give tricarbonyl(cyclopentadienyl)rhenium derivatives with high yields.

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available in the form of the perrhenate.^[8] It is for this reason

Introduction

The $[\text{Re}(\text{CO})_6]^+$ cation is a robust compound insensitive to air or moisture. It is normally prepared by one of two different standard preparation methods, either by reaction of Re(CO)₅X with AlCl₃ under high pressure of CO gas,^[1] or by treating ethyl chloroformate with Re(CO)₅Na at normal atmospheric pressure, followed by addition of BF₃.^[2] Unlike Re₂(CO)₁₀, Re(CO)₅Br or [Re(CO)₅]⁻, precursors that are often used as reagents in the synthesis of carbonyl complexes of Re, $[Re(CO)_6]^+$ is normally considered to be a relatively inert compound. To the best of our knowledge only a few rare studies have dealt with its reactivity. One example is the nucleophilic reaction with the azide ion or amines, leading to the formation of the isocvanate Re-(CO)₅(NCO) and of the amide Re(CO)₅(CONRR'), respectively.^[3] The carbonyl ligands are labile in this cation, and up to three CO groups can be substituted by two-electron donor ligands, such as triphenylphosphane.^[4] It is also known that $[\operatorname{Re}(\operatorname{CO})_6]^+$ reacts with the metallate anions [Fe(CO)₄]²⁻, [Mn(CO)₅]⁻, [W(CO)₅Cl]⁻ and [W(CO)₅H]⁻ by an electron-transfer reaction to give $[Re(CO)_5]^-$, (CO)₅MnRe(CO)₅, Re(CO)₅Cl and HRe(CO)₅, respectively.^[5] [Re(CO)₆]⁺ possesses several properties that are worth exploiting. Firstly, its solubility and stability allow it to be used in aqueous media. Secondly, it has been shown that hexacarbonyltungsten is accessible in its radioactive form $^{188}W(CO)_6$ and that its disintegration should lead to the formation of $[^{188}\text{Re}(\text{CO})_6]^+$ and $[^{188}\text{Re}(\text{CO})_5]^{\cdot,[6]}$ This transformation is an important one, since ¹⁸⁶Re and ¹⁸⁸Re are now recognized as radionuclides with therapeutic applications.^[7] At present, the radionuclide of rhenium is only

that rhenium-based radiopharmaceuticals have normally been prepared as chelates of the N_2S_2 or N_3S type.^[9] The need for new radiopharmaceuticals with good stability has led us to consider the idea of using the tricarbonyl(cyclopentadienyl)rhenium group in place of the chelates, since it has the advantages of being lipophilic, less bulky and more robust.^[10] The concept of using carbonyl organometallic compounds as radiopharmaceuticals is undergoing rapid expansion.[11] However, syntheses of cyclopentadienyl complexes of Re require multi-step reactions. The traditional methods are not available for radionuclides of rhenium. The search for an efficient preparation method has led us to propose a new synthesis for certain rhenium compounds, including Re₂(CO)₁₀ at normal atmospheric pressure,^[12] and $(\eta^5-C_5H_4COOH)Re(CO)_3$ by a simple thermal reaction of $\text{Re}_2(\text{CO})_{10}$.^[13] Other synthetic advances have been made by Katzenellenbogen et al.^[14] and by Alberto et al.^[15] Recently, Alberto demonstrated the viability of preparing cyclopentadienyltechnetium complexes in aqueous media using the reagent $[Tc(CO)_3(H_2O)_3]^+$ obtained from radioactive pertechnetate.^[16] However, this synthesis is limited for the moment to cyclopentadienyl compounds bearing a carbonyl substituent. There is therefore a clear need for a new source of radioactive rhenium to widen the range of organometallic radiopharmaceuticals. With this aim in mind, $[^{188}\text{Re}(\text{CO})_6]^+$ could be generated by the decay of $^{188}W(CO)_6$, thus providing a solution to the problem and an interesting alternative to the ¹⁸⁸ReO₄⁻ generator based on $^{188}WO_3$.^{[8] 188}W(CO)₆ decay should clearly be the most direct route to the production of the carbonyl rhenium reagent. It has already been clearly established that $[^{99m}Tc(CO)_6]^+$ can be obtained from $^{99}Mo(CO)_6$.^[17] This β decay of 99Mo is interesting owing to the imaging application of ^{99m}Tc as well as the recognized similarity between the chemistry of Re and Tc. We were therefore interested in examining the potential of $[\text{Re}(\text{CO})_6]^+$ in the synthesis of

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organometallic complexes. The double ligand-transfer reaction was a particular object of study with a view to preparing radiopharmaceuticals. This reaction, first reported by Wenzel,^[18] has recently been enhanced by Katzenellenbogen et al.^[14] We also showed that $\text{Re}_2(\text{CO})_{10}$ can be used in ligand-transfer reactions with cyclopentadienyl complexes.^[19] It may therefore be possible to use the $[\text{Re}(\text{CO})_6]^+$ cation in this type of ligand transfer. We describe here the first results obtained with this cation.

Results and Discussion

Acetylferrocene was chosen for our first experiments with $[\text{Re}(\text{CO})_6]^+$ since this complex has been found to give the best results in ligand-exchange reactions.^[14]



Scheme 1. Ligand-transfer reaction between acetylferrocene and hexacarbonylrhenium cation

Scheme 1 shows the synthetic route that was used. Acetylferrocene, [Re(CO)₆][BF₄] and methanol were placed in a sealed tube and heated to 170 °C. After heating for 1 h purification by chromatography, $(\eta^5-C_5H_4CO$ and Me)Re(CO)₃ was obtained in 30% yield. We note that $CpRe(CO)_3$ is not formed under these reaction conditions. The low yield is probably due to the poor solubility of [Re(-CO)₆[[BF₄] in methanol. Since this compound is very soluble in DMSO and DMF, the experiment was therefore repeated with DMSO in place of methanol as solvent. Owing to the high boiling point of DMSO, it was not necessary to use a sealed tube. A solution of acetylferrocene and [Re(- CO_{6} [BF₄] in commercial DMSO was heated in an oil bath at 160 °C for 30 min. In this case, a 70% yield of ($\eta^{5}\text{-}$ C₅H₄COMe)Re(CO)₃ was obtained. DMSO was later replaced with DMF. Under the same conditions (η^{5} - $C_5H_4COMe)Re(CO)_3$ was isolated in 64% yield. The choice of solvent has a clear influence on the outcome of the reaction. To elucidate this point, we carried out the experiments with other common solvents, such as acetonitrile, acetone, ethanol as well as water. Experimental conditions and yields obtained are summarized in Table 1.

[Re(CO)₆][BF₄] is also soluble in acetonitrile. Heating a solution of the cation in acetonitrile at 95 °C for 27 h gave neither (η^5 -C₅H₄COMe)Re(CO)₃ nor CpRe(CO)₃. The experiment was repeated using a maximum temperature of 160 °C in a sealed tube. Again, no cyclopentadienylated complex was formed, and only [Re(CO)₃(MeCN)₃]⁺ was isolated. Heating the solution to boiling point in acetone or ethanol also failed to give (η^5 -C₅H₄COMe)Re(CO)₃.

We also tried to conduct the reaction in aqueous media, because this solvent is the most commonly used for radiopharmaceutical syntheses.^[16] Heating a solution of the $[Re(CO)_6]^+$ cation and acetylferrocene in water at 95 °C for 2 h gave neither (η^5 -C₅H₄COMe)Re(CO)₃ nor CpRe(CO)₃. On the other hand, the same reaction carried out in a pressure tube gave rise to (η^5 -C₅H₄COMe)Re(CO)₃ in 13% yield. The result is even more promising in a pressure tube with a water/DMSO (1:1) mixture: in this case a yield of 60% of (η^5 -C₅H₄COMe)Re(CO)₃ was obtained. The use of the [Re(CO)₆]⁺ cation in a water-based mixture of solvents could thus be envisaged. It is essential to consider this aspect when radioactive elements are handled.

The results reported below show that temperature also has a significant effect on the reaction. To study this effect, the exchange reaction was repeated using DMSO and DMF as solvents at different temperatures. The results obtained are listed in Table 2.

In DMSO, the yield of $(\eta^5-C_5H_4COMe)Re(CO)_3$ drops from 70% to 58% and then to 16% when the temperature is lowered from 160 °C to 130 °C and then 90 °C, even when the reaction is allowed to proceed for a longer time. The same pattern is observed with DMF, in which case the yield drops from 64% to 23%, and finally to 0%. This result indicates that the reaction with [Re(CO)₆][BF₄] requires heating to approximately 160 °C to obtain the rhenium tricarbonyl complex in good yield.

Table 1. Reaction of acetylferrocene with [Re(CO)₆][BF₄] in a variety of solvents

Entry	Solvent	Quantity of acetylferrocene	Heating time	Temperature of heating bath	Yield of (η ⁵ -C ₅ H ₄ COMe)Re(CO) ₃
1	DMSO	3.12 equiv.	30 min	160 °C	70%
2	DMF	3.12 equiv.	30 min	160 °C	64%
3	MeOH ^[a]	3.12 equiv.	1 h	170 °C	30%
4	MeOH	3.12 equiv.	17 h	95 °C (reflux)	0%
5	H ₂ O	3.12 equiv.	2 h	110 °C (reflux)	0%
6	$H_2O^{[a]}$	3.12 equiv.	1 h	160 °C	13%
7	H ₂ O/DMSO (1:1) ^[a]	3.12 equiv.	1 h	160 °C	60%
6	MeCN	1.05 equiv.	27 h	95 °C (reflux)	0%
7	acetone	1.05 equiv.	17 h	75 °C (reflux)	0%
8	EtOH	3.12 equiv.	17 h	95 °C (reflux)	0%

^[a] Reaction under pressure in a sealed tube.

Table 2.	Reaction	of a	acetylferrocene	with	$[\text{Re}(\text{CO})_6][\text{BF}_4]$ in DMSO and DMF

Entry	Solvent	Quantity of acetylferrocene	Heating time	Temperature of heating bath	Yield of (η ⁵ -C ₅ H ₄ COMe)Re(CO) ₃
1	DMSO	3.12 equiv.	30 min	160 °C	70%
2	DMSO	3.12 equiv.	3 h	130 °C	62%
3	DMSO	1.05 equiv.	4 h 30	130 °C	58%
4	DMSO	3.12 equiv.	5 h 30	90 °C	16%
5	DMF	3.12 equiv.	30 min	160 °C	64%
6	DMF	1.05 equiv.	3 h	160 °C	71%
7	DMF	1.05 equiv.	3 h	130 °C	23%
8	DMF	1.05 equiv.	4 h 30	90 °C	0%

Table 3. Reaction of $(\eta^5-C_5H_4R)$ FeCp with [Re(CO)₆][BF₄] in DMSO

Entry	R	Quantity of $(\eta^5-C_5H_4R)FeCp$	Heating time	Temperature of heating bath	Yield of $(\eta^5-C_5H_4R)Re(CO)_3$
1	COMe	1.05 equiv.	4 h 30	130 °C	58%
2	Н	3.56 equiv.	5 h	180 °C	18%
3	COH	1.05 equiv.	30 min	160 °C	12%
4	COH	1.05 equiv.	3 h 20	130 °C	33%
5	COOEt	1.05 equiv.	2 h 30	160 °C	34%
6	C≡CH	1.05 equiv.	1 h 30	160 °C	0%

We also assessed how the nature of the ferrocene substituent might influence the reaction. Ferrocene, formylferrocene, ethyl ferrocenecarboxylate and ethynylferrocene were all tested in reactions in DMSO. Yields and experimental conditions are shown in Table 3.

Ferrocene gives 18% CpRe(CO)₃ after 5 h of heating at 180 °C. Formylferrocene and ethyl ferrocenecarboxylate give 33% and 34%, respectively of tricarbonyl(cyclopentadienyl)rhenium derivatives. Ethynylferrocene, however, gives (η^5 -C₅H₄COMe)Re(CO)₃ in 48% yield instead of the expected (η^5 -C₅H₄C≡CH)Re(CO)₃. This type of transformation was also observed in the reaction with the perrhenate.^[14] The reaction with [Re(CO)₆][BF₄] was also tested with a fairly complex molecule such as *N*-phenylferrocene-carboxamide (Scheme 2).



Scheme 2. Ligand-transfer reaction between *N*-phenylferrocenecarboxamide and hexacarbonylrhenium cation

Heating a solution of $[Re(CO)_6][BF_4]$ and *N*-phenylferrocenecarboxamide to 160 °C for 3 h gives tricarbonyl(*N*phenylcyclopentadienylcarboxamide)rhenium in 43% yield.

The results obtained clearly show that $[Re(CO)_6][BF_4]$ does not react in the same way as the perrhenate.^[14] The

one-pot reaction between ReO₄⁻ and acetylferrocene in the presence of Cr(CO)₆ and CrCl₂ does not lead to the expected product in DMSO or in DMF. For this double ligand-transfer reaction, methanol was the only solvent that provided $(\eta^5-C_5H_4COMe)Re(CO)_3$ in acceptable yield (65%). This difference might be attributed to the fact that the reduction or the carbonyl transfer did not seem to proceed very well in DMSO or in DMF. By contrast, in our case, the best yields were obtained with DMSO or DMF, while methanol gave only mediocre results. It should be noted that $[Re(CO)_6][BF_4]$ is the only reagent that can react with ferrocene itself, while the perrhenate^[14] and $\text{Re}_2(\text{CO})_{10}$ ^[13] are inactive. To identify the real intermediate of the reaction, the [Re(CO)₆][BF₄] solution in DMSO was heated to 80 °C for 3 h. The progress of the reaction was monitored using IR spectroscopy. A progressive disappearance of the peak at 2071 cm⁻¹ of [Re(CO)₆][BF₄] and concomitant progressive formation of two peaks at 2021 cm⁻¹ and 1893 cm⁻¹ were observed, characteristic of a molecule possessing C_{3v} symmetry. We postulate the formation of $[Re(CO)_3(DMSO)_3]^+$. The same transformation was also noted when [Re(CO)₆][BF₄] was heated in DMF or acetonitrile under pressure. In this last case, it was possible to isolate the $[Re(CO)_3(MeCN_3)]^+$ cation which was identified by IR data.^[20] Consequently, we propose that our reaction occurs in two stages (Scheme 3).

The first is the replacement of the three CO groups with solvent molecules. This exchange occurs at around 80 °C. The second step is the reaction between $[\text{Re}(\text{CO})_3(\text{L})_3]^+$ and the ferrocene derivative. This final reaction only begins around 130 °C and reaches full efficiency at 160 °C. Based on literature work, it has been suggested that the $\eta^5 - \eta^3$ slippage of the Fe-cyclopentadienyl bond of the ferrocene



Scheme 3. Possible mechanism of cyclopentadienyl transfer reaction

derivative is responsible for its reaction with [Re(CO)3-(MeO)(MeOH)₂].^[14] It has also been observed that the ferrocene derivative reacts with [(naphthalene)- $Mn(CO)_3]BF_4$ via the dimetallic intermediate [Cp-Fe-Cp'-Mn(CO)₃]⁺.^[21] Two mechanistic possibilities thus spring to mind for the reaction with $[\text{Re}(\text{CO})_3(\text{L})_3]^+$. The first is the $\eta^5 - \eta^3$ slippage of the Fe-cyclopentadienyl bond, allowing the formation of the intermediate I which is converted into the tricarbonylrhenium compound. The second possibility is formation of the dimetallic intermediate II, followed by breaking of the Fe-Cp' bond. Sweigart has shown that heating to 40 °C in dichloromethane is sufficient to cause [(naphthalene)Mn(CO)₃]BF₄ to react with a ferrocene derivative, leading to formation of tricarbonyl(cyclopentadienyl)manganese. Heating $[\text{Re}(\text{CO})_3(L)_3]^+$ with the ferrocene compound to a high temperature is thus necessary to change the hapticity of the cyclopentadienyl ligand (intermediate I), or to drive off the three solvent molecules (intermediate II). Without proof of the formation of intermediates I and II, it is difficult at this stage to suggest a precise mechanism. However, the acetyl group on the cyclopentadienyl ring, acting as an electron-withdrawing group, should minimize the formation of the intermediate II. It is noteworthy that the reaction under pressure, using acetonitrile as the solvent, stops only at the point where $[Re(CO)_3(Me_3CN)_3]^+$ is formed indicating that this intermediate is not sufficiently reactive in the ligand-transfer reaction. To summarize, $[Re(CO)_3(Me_3CN)_3]^+$ is not an efficient intermediate, but its existence is a valuable mechanistic indicator suggesting future directions in the use of $[\text{Re}(\text{CO})_6]^+$.

Conclusion

We have shown for the first time that the $[\text{Re}(\text{CO})_6]^+$ cation reacts with ferrocene derivatives through a ligand-transfer reaction to give tricarbonyl(cyclopentadienyl)rhenium

complexes. The reaction is rapid and in certain cases gives good yields. Due to its reactivity in water and its potential availability in a radioactive form, this reagent could be used for synthesis in water, and also in radiopharmaceutical syntheses. The reaction with $[\text{Re}(\text{CO})_6]^+$ is both simpler and cleaner than that with the perrhenate, which requires a CO source and high pressure. We are continuing to study other types of reactions with this cation.

Experimental Section

General: The synthesis of all the compounds was performed under ambient atmospheric conditions. DMSO was used without any purification. TLC chromatography was performed on silica gel 60 GF254. Infrared spectra were obtained with an IR-FT BOMEM Michelson-100 spectrometer. ¹H and ¹³C NMR spectra were recorded with 200 MHz and 400 MHz Bruker spectrometers. Mass spectrometry was performed with a Nermag R 10-10C spectrometer. Melting points were measured with a Kofler device. Elemental analyses were performed by the regional microanalysis department of the Université Pierre et Marie Curie.

Hexacarbonylrhenium: [Re(CO)₆][BF₄] was prepared according to the procedure described in the literature.^[2] IR (CH₃CN): $\tilde{\nu} = 2085$ (ν_{CO}) cm⁻¹.

Synthesis of (Acetylcyclopentadienyl)tricarbonylrhenium in DMSO and in DMF: [Re(CO)₆][BF₄] (0.073 g, 0.166 mmol) was dissolved in DMSO (1 mL) in a 5-mL round-bottom flask equipped with a magnetic stirrer bar. Acetylferrocene (0.040 g, 0.175 mmol) was added and the solution heated for 4 h 30 min at 130 °C. The mixture was allowed to warm to room temperature and then 10 mL of water was added. The product was extracted with dichloromethane (2 \times 50 mL). The organic phase was washed, dried (MgSO₄), filtered and concentrated. The mixture was purified by chromatography on a silica gel plate (petroleum ether/ethyl acetate, 7:1) to give (acetylcyclopentadienyl)tricarbonylrhenium (0.036 g, 58%). ¹H NMR (200 MHz, CDCl₃): $\delta = 2.34$ (s, 3 H, CH₃), 5.40 (t, J = 2.2 Hz, 2 H, 3,4-H of C_5H_4), 5.98 (t, J = 2.2 Hz, 2 H, 2,5-H of C_5H_4) ppm. IR (CH₂Cl₂): $\tilde{v} = 2032$ s, 1939 s (v_{CO}), 1688 w (COCH₃) cm⁻¹. By using DMF as solvent and by applying the same procedure (heating time: 3 h), 23% yield of (acetylcyclopentadienyl)tricarbonylrhenium was obtained.

Synthesis of (Acetylcyclopentadienyl)tricarbonylrhenium under Pressure: [Re(CO)₆][BF₄] (0.073 g, 0.166 mmol) and acetylferrocene (0.118 g, 0.519 mmol) were combined in a 20-mL pressure tube containing a magnetic stirrer bar. Methanol (1 mL) was added, and the tube was sealed and heated to 170 °C. After the heating period, the tube was cooled to room temperature. The solvent was evaporated, the mixture was dissolved in a minimum volume of CH_2Cl_2 and purified by chromatography on a silica gel plate (petroleum ether/ethyl acetate, 7:1) to give (acetylcyclopentadienyl)tricarbonylrhenium (0.020 g, 30%).

Ethyl Ferrocenecarboxylate: Ferrocenecarboxylic acid (0.500 g, 2.17 mmol) was dissolved in ethanol (12 mL) in a 25-mL roundbottom flask equipped with a magnetic stirrer bar. H_2SO_4 (0.15 mL) was added, and the solution heated under reflux for 12 h. The mixture was allowed to cool to room temperature and the solvent was partially evaporated. Cold water (10 mL) was added and the product was extracted with diethyl ether (3 × 100 mL). The organic phase was washed first with saturated K_2CO_3 solution, to eliminate the excess acid, and then with water. The organic phase was dried (MgSO₄), filtered and concentrated. The mixture was purified by chromatography on a silica gel plate (petroleum ether/ ethyl ether, 4:1) to give ethyl ferrocenecarboxylate (0.108 g, 19%). ¹H NMR (200 MHz, CDCl₃): $\delta = 1.37$ (t, J = 7.1 Hz, 3 H, CH₃), 4.21 (s, 5 H, Cp), 4.29 (q, J = 7.1 Hz, 2 H, O-CH₂-), 4.40 (t, J = 1.9 Hz, 2 H, 3,4-H of C₅H₄), 4.82 (t, J = 1.9 Hz, 2 H, 2,5-H of C₅H₄) ppm. MS (EI): m/z = 258 [M]⁺, 230 [M - C₂H₄]⁺, 138, 121, 56 [Fe]⁺.

N-Phenylferrocenecarboxamide: The reaction was carried out under argon in a Schlenk tube equipped with a reflux condenser. Ferrocenecarboxylic acid (0.152 g, 0.66 mmol) was placed into the Schlenk tube and cooled with an ice bath. Oxalyl chloride (3 mL, 34 mmol) was then added and the solution was kept at room temperature for 2 h. The oxalyl chloride was evaporated. The acyl chloride formed was dissolved in anhydrous THF (4 mL), and aniline (0.186 g, 2 mmol) was added dropwise. The mixture was stirred for 3 h then separated by chromatography on a silica gel plate (petroleum ether/dichloromethane, 1:1) to give N-phenylferrocenecarboxamide (0.114 g, 57%) m.p. 211 °C. ¹H NMR (200 MHz, $(CD_3)_2CO$: $\delta = 4.24$ (s, 5 H, Cp), 4.42 (dd, J = 1.9 Hz, 2 H, 3,4-H of C_5H_4), 4.97 (dd, J = 1.9 Hz, 2 H, 2,5-H of C_5H_4), 7.05 (m, 1 H, Ph), 7.31 (m, 2 H, Ph), 7.76 (m, 2 H, Ph), 8.84 (s, 1 H, NH) ppm. ¹³C NMR (50 MHz, (CD₃)₂CO): δ = 73.7, 74.6, 75.5, 77.8, 120.8, 123.9, 129.4, 140.5, 168.9 (CO) ppm. MS (EI): m/z = 305[M]⁺, 213 [CpFeC₅H₄CO]⁺, 185 [FeCp₂]⁺, 65 [Cp]⁺. C₁₇H₁₅FeNO (305.16): calcd. C 66.91, H 4.95, N 4.59; found. C 66.70, H 5.27, N 4.39.

Reaction in Water and in Water/DMSO: [Re(CO)₆][BF₄] (0.073 g, 0.166 mmol) and acetylferrocene (0.118 g, 0.519 mmol) were combined in a 20-mL pressure tube containing a magnetic stirrer bar. Water (1 mL) was added, then the tube was sealed and heated to 160 °C. After heating for 1 h, the tube was cooled to room temperature. 10 mL of water was added. The product was extracted with dichloromethane (2×50 mL). The organic phase was dried (MgSO₄), filtered and concentrated. The mixture was purified by chromatography on a silica gel plate (petroleum ether/ethyl acetate, 7:1) to give (acetylcyclopentadienyl)tricarbonylrhenium (0.008 g, 13%). By using a water/DMSO mixture (0.5 mL/0.5 mL) as solvent and by applying the same procedure, 60% yield of (acetylcyclopentadienyl)tricarbonylrhenium.

Reaction in Acetonitrile: [Re(CO)₆][BF₄] (0.073 g, 0.166 mmol) and acetylferrocene (0.040 g, 0.175 mmol) were combined in a 20-mL pressure tube containing a magnetic stirrer bar. Acetonitrile (1 mL) was added, then the tube was sealed and heated to 170 °C. After the heating period, the tube was cooled to room temperature. The solvent was evaporated, the mixture was dissolved in a minimum volume of CH₂Cl₂ and purified by chromatography on a silica gel plate (petroleum ether/ethyl acetate, 7:1) to give $[\text{Re}(\text{CO})_3(\text{CH}_3\text{CN})_3]^+$ (0.042 g). IR (CH₂Cl₂): $\tilde{v} = 2053$ s, 1953 s (v_{CO}) cm⁻¹.

Reaction with Ferrocene: The procedure is similar to that of the synthesis of (acetylcyclopentadienyl)tricarbonylrhenium in DMSO. Ferrocene (0.110 g, 0.591 mmol) was used in a reaction heated for 5 h at 180 °C. The compound was purified on a silica gel plate (petroleum ether/ethyl acetate, 20:1) to give tricarbonyl(cyclopentadienyl)rhenium (0.010 g, 18%). ¹H NMR (200 MHz, CDCl₃): $\delta = 5.38$ (s, 5 H, Cp) ppm. IR (CH₂Cl₂): $\tilde{\nu} = 2024$ s, 1926 vs (v_{CO}) cm⁻¹.

Reaction with (N-Phenyl)ferrocenecarboxamide: The procedure is similar to that of the synthesis of (acetylcyclopentadienyl)tricarbonylrhenium in DMSO. N-phenylferrocenecarboxamide (0.054 g, 0.175 mmol)was used and the reaction mixture was heated for 3 h at 160 °C. The compound was purified by chromatography on a silica gel plate (ethyl acetate/petroleum ether, 2:1) to give tricarbonyl(N-phenylcyclopentadienylcarboxamide)rhenium (0.032 g, 43%), m.p. 179 °C. ¹H NMR (200 MHz, (CD₃)₂CO): $\delta = 5.72$ (t, J =2.3 Hz, 2 H, 3,4-H of C₅H₄), 6.41 (t, J = 2.3 Hz, 2 H, 2,5-H of C_5H_4), 7.10 (m, 1 H, Ph), 7.32 (m, 2 H, Ph), 7.67 (m, 2 H, Ph), 9.25 (s, 1 H, -NH-CO) ppm. ¹³C NMR (100 MHz, (CD₃)₂CO): $\delta = 86.6 (C_{Cp}), 88.1 (C_{Cp}), 96.5 (C_{Cp}), 120.9 (C_{Ar}), 124.7 (C_{Ar}),$ 129.4 (CAr), 139.3 (CAr), 161.0 (NHC=O), 194.1 (CO) ppm. IR (CH₂Cl₂): $\tilde{\nu}$ = 2033 s, 1945 s (ν_{CO}) cm⁻¹. MS (EI): *m*/*z* = 455 $[M]^+$, 427 $[M - CO]^+$, 371 $[M - 3CO]^+$. $C_{15}H_{10}NO_4Re$ (454.45): calcd. C 39.64, H 2.22, N 3.08; found. C 40.05, H 2.00, N 3.00.

Reaction with Formylferrocene: The procedure is similar to that of the synthesis of (acetylcyclopentadienyl)tricarbonylrhenium in DMSO. Formylferrocene (0.038 g, 0.175 mmol) was used in a reaction that underwent 3 h 20 min of heating at 130 °C. The compound was purified by chromatography on a silica gel plate (petroleum ether/ethyl acetate, 5:1) to give tricarbonyl(formylcyclopentadienyl)rhenium (0.020 g, 33%). ¹H NMR (200 MHz, CDCl₃): $\delta = 5.5$ (t, J = 2.4 Hz, 2 H, 3,4-H of C₅H₄), 6.0 (t, J = 2.4 Hz, 2 H, 2,5-H of C₅H₄), 9.59 (s, 1 H, -COH) ppm. IR (CHCl₃): $\tilde{v} = 2036$ s, 1945 s ($v_{\rm CO}$), 1693 w (-CHO) cm⁻¹. IR (KBr): $\tilde{v} = 2031$ s, 1920 s ($v_{\rm CO}$), 1690 w (-CHO) cm⁻¹. MS (EI): m/z = 364 [M]⁺, 336 [M - CO]⁺, 308 [M - 2 CO]⁺, 280 [M - 3 CO]⁺. Also isolated was Re₂(CO)₁₀ (0.005 g, 4%). IR (CHCl₃): $\tilde{v} = 2071$ w, 2014 vs ($v_{\rm CO}$), 1971 w cm⁻¹.

Reaction with Ethyl Ferrocenecarboxylate: The procedure is similar to that of the synthesis of (acetylcyclopentadienyl)tricarbonylrhenium in DMSO. Ethyl ferrocenecarboxylate (0.045 g, 0.175 mmol) was used in a reaction that underwent 2 h 30 min of heating at 160 °C. The compound was purified by chromatography on a silica gel plate (petroleum ether/ethyl ether, 4:1) to give tricarbonyl(ethoxycabonylcyclopentadienyl)rhenium (0.023 g, 34%). ¹H NMR (200 MHz, CDCl₃): $\delta = 1.32$ (t, J = 7.1 Hz, 2 H, CH₃), 4.28 (q, J = 7.1 Hz, 2 H, OCH₂), 5.37 (t, J = 2.3 Hz, 2 H, 3,4-H of C₅H₄), 6.02 (t, J = 2.3 Hz, 2 H, 2,5-H of C₅H₄) ppm. IR (CHCl₃): $\hat{v} = 2033$ s, 1945 s (v_{CO}), 1722 w (-CO-OEt) cm⁻¹. MS (EI): m/z = 408 [M]⁺, 380 [M - CO]⁺, 352 [M - 2 CO]⁺, 324 [M - 3 CO]⁺, 308, 268, 225.

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