ELECTROCHEMISTRY OF PHOSPHAFERROCENES

II*. ELECTROCHEMICAL BEHAVIOR OF 3,3',4,4'-TETRAMETHYL-1,1'-DIPHOSPHAFERROCENE BONDED TO M(CO)₅ (M = Cr, Mo, W) FRAGMENTS FORMING HETEROMETALLIC COMPLEXES WITH MULTIPLE REDOX CENTERS

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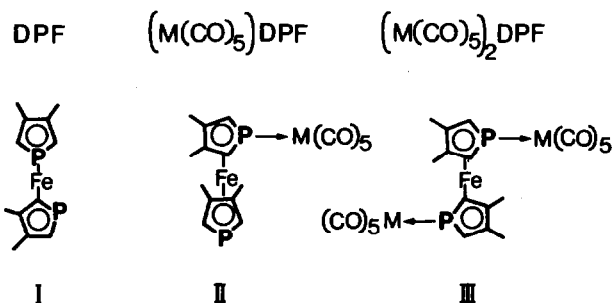
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Summary

The redox behaviour of a series of heterometallic phosphaferrocenes (hereafter refered to as I, II and III) has been studied in propylene carbonate containing 0.1 M $(C_2H_5)_4N^+ ClO_4^-$ at both mercury and platinum electrodes.

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* For part I see ref. 1.

Complex I (DPF) undergoes a reversible one-electron reduction. Complexes II and III exhibit the same reversible reduction step and one (species II) or two (species III) additional irreversible reduction step(s) generating $[M(CO)_5]^-$ anions (M = Cr, Mo, W).

Oxidation of the complexes II and III indicates that fragment I is involved in the first, easiest, oxidation step, whereas further step(s) involve the $M(CO)_5$ moieties. The redox characteristics of the complexes I, II, III, clearly indicate the absence of cooperation between metallic centers in II and III and the very effective barrier provided by the central iron in moiety I towards mutual effects of both phospholyl rings.

Introduction

Organometallic complexes containing several transition metals forming multiple redox centers are of considerable interest at the present time [2,3]. Complexes of this type whose electrochemistry has been studied possess metal–metal bonds, as in clusters [2], or are only weakly coupled systems [3]. The synthesis and spectroscopic properties of some complexes of I* have been recently described [4]. We have studied the electrochemical behavior of I, its monometallic metal carbonyl complexes, II, and its bimetallic metal carbonyl complexes III, and report the results herein.

DPF   (M(CO)$_5$)DPF   (M(CO)$_5$)$_2$DPF

(I)   (II)   (III)

M = Cr, Mo, W
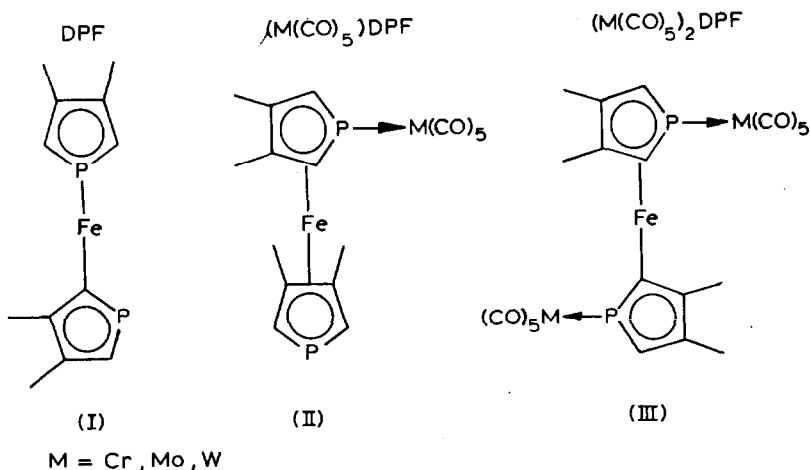
Results

The complexes II and III may be regarded either as substituted diphosphaferrocenes or as substituted metal carbonyls $LM(CO)_5$, where L is I or II, respectively. Since the aim of the present study is to evaluate the role of each metallic fragment and to assess its contribution to the global electrochemical behavior of the complex, it is necessary first to consider the electrochemistry of the isolated fragments for purposes of comparison.

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* 3,3′,4,4′-Tetramethyl-1,1′-diphosphaferrocene (DPF) [4].

TABLE 1

REDOX POTENTIALS [5,6] FOR $M(CO)_6$ AND $M(CO)_5S$ ON PLATINUM AND MERCURY ELECTRODES (S = DMF, Propylene carbonate, CH_3CN), DETERMINED BY CYCLIC VOLTAMMETRY (0.3 V s^{-1}) ON Pt ELECTRODE (oxidation) AND NORMAL PULSE POLAROGRAPHY ON A DROPPING MERCURY ELECTRODE (reduction) (All steps are one-electron transfers)

$E_{1/2}{}^a$ V/SCE	$Cr(CO)_6$	$Cr(CO)_5S$	$Mo(CO)_6$	$Mo(CO)_5S$	$W(CO)_6$	$W(CO)_5S$
Reduction						
S = DMF	−2.15	−1.69	−2.01	−1.68	−1.91	−1.70
S = PC	−2.28	−2.00	−2.12	−2.00	−2.03	−1.93
S = CH_3CN	−2.37	−2.04	−2.20	−2.00	−2.07	−1.92
Oxidation						
CH_3CN	+1.46	–	+1.56	–	+1.62	+1.12

^{a} Potentials are in V vs. SCE (saturated calomel electrode). Reduction potentials were recorded on DME (dropping mercury electrode) whereas oxidation was studied on a Pt RDE (rotating disc electrode 2000 rpm, 3.14 mm^2). Supporting electrolyte: 0.1 M $(C_2H_5)_4NClO_4$.

Electrochemical behavior of $M(CO)_6$ and $M(CO)_5S$

The electrochemical properties of $M(CO)_6$ and $M(CO)_5S$ (M = Cr, Mo, W; S = CH_3CN, DMF, propylene carbonate) have been previously studied (Table 1). Each of the $M(CO)_6$ complexes was found to undergo an irreversible one-electron reduction [5,6] in propylene carbonate with the half-wave reduction potentials sequence (V vs. SCE) $W(CO)_6$ (−2.03 V) > $Mo(CO)_6$ (−2.12 V) > $Cr(CO)_6$ (−2.28 V).

Replacement of one of the CO groups by a stronger σ donor such as CH_3CN, dimethylformamide (DMF) or propylene carbonate (PC) unexpectedly shifted the reduction potentials anodically (Table 1), and an explanation is given in the discussion. In CH_3CN containing 0.1 M $(C_2H_5)_4NClO_4$ TEAP, the oxidation potential sequence (V vs. SCE) for the following series $W(CO)_6$ (+1.62 V) > $W(CO)_5CH_3CN$ (+1.12 V) > $W(CO)_4 \cdot (CH_3CN)_2$ (+0.65 V) was in accordance with the expected facilitation of the oxidation by the donor ligand CH_3CN. A similar trend was observed when carbonyl were replaced by isonitrile ligands in $M(CO)_6$ complexes [12].

Electrochemical behavior of I

The compound I (DPF) undergoes a reversible one-electron reduction at $E_{1/2} = -2.33$ V vs. SCE and a one-electron oxidation at $E_{1/2} = +0.53$ V vs. SCE in propylene carbonate on mercury electrode (Table 2) [1]. This complex I is easier to reduce than ferrocene by about 0.60 V and more difficult to oxidize than ferrocene by about 0.10 V. This is an overall consequence of both the replacement of CH groups by electron-withdrawing P atoms (net result of poor σ-donor and good π-acceptor phosphorous atom in I [4]) and the addition of electron-donating methyl groups to the ring [1]. The first oxidation of complex I occurs by an EC mechanism due to the low stability of the I$^+$ cation and the electrochemical behavior of I is solvent dependent [1]. The species I also undergoes a second irreversible two-electron oxidation at $E_{1/2}$ +1.8 V vs. SCE.

Electrochemical behavior of complexes II and III on mercury electrodes

Table 2 presents the reduction and oxidation potentials for the studied com-

TABLE 2 [a]

OXIDATION–REDUCTION POTENTIALS OF THE STUDIED PHOSPHAFERROCENES

Compound	Oxidation		Reduction [b]
	$E_{1/2}^{anod}$ on DME V/SCE ±0.01	E_{peak}^{anod} on Pt RDE 0.05 V/s V/SCE ±0.01	$E_{1/2}^{cathod}$ on DME V/SCE ±0.01
Ferrocene	+0.43 rev	+0.40	−2.93 [c] rev
I DPF	+0.53 irr	+0.57 rev	−2.33 rev
II [Cr(CO)$_5$]DPF	+0.70 irr	+0.55; +1.00	−1.78 irr, −2.36 rev
III [Cr(CO)$_5$]$_2$DPF		+0.70; +0.93; +1.10	−1.66 irr, −1.78 irr, −2.38 rev
II [Mo(CO)$_5$]DPF	+0.70 irr	+0.65; +1.15	−1.80 irr, −2.36 rev
III [Mo(CO)$_5$]$_2$DPF		+0.79; +0.97; +1.11	−1.68 irr, −1.83 irr, −2.38 rev
II [W(CO)$_5$]DPF	+0.71 irr	+0.76; +1.25	−1.75 irr, −2.36 rev
III [W(CO)$_5$]$_2$DPF		+0.74; +0.87; +1.17	−1.65 irr, −1.75 irr, −2.38 rev

[a] PC+0.1 M TEAP. [b] All steps: 1 ē. [c] DMF+0.2 M Bu$_4$Ni at −10°C [9].

pounds. All the reductive charges-transfers were diffusion controlled (i_{lim} = f(c) and (i_p = f($v^{1/2}$)) being of straight lines crossing the origin of the axis).

Compared to I, complexes II and III exhibit between −1.7 and −1.9 V (Fig. 1) an additional one-electron reduction as indicated by controlled potential coulometry (see below). This step is irreversible and occurs at a potential near that for the reduction of M(CO)$_5$DMF (Table 1). Furthermore the reduction pattern of complexes III differs from the reduction of complexes II by the presence of an additional reduction step between −1.65 and −1.68 V which is less cathodic than either of the two reduction steps observed for II. In normal pulse polarography, all three reductions of complex III show limiting currents of the same magnitude. The
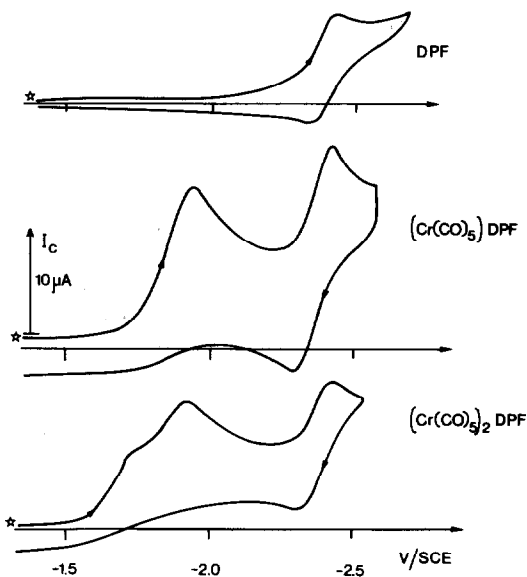

Fig. 1. Reduction of DPF, [Cr(CO)$_5$]DPF, [Cr(CO)$_5$]$_2$DPF: Cyclic voltammetry on a mercury electrode v 10 V/s in propylene carbonate containing 0.1 M TEAP, c ≈ 5×10^{-4} M. *Start of the scan.

additional reduction step observed near -2.3 V for both compounds II and III is attributable to the reduction of the fragment I in these complexes, and the potential of this reversible reduction differs only slightly from the reduction potential of the free species I.
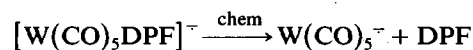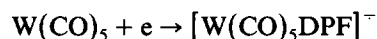
Cyclic voltammetry analysis of these reduction steps revealed that the first reduction of II (between -1.70 and -1.80) as well as the first two reductions of III, are followed by chemical decomposition of the primary reduction products. In addition, after these chemical decompositions reactions occurred in reduced solutions, $[M(CO)_5]^-$ (M = Cr, Mo, W) anions were identified in solution from their reoxidation potentials, already known from previous studies [5].

The ^{31}P NMR spectra on solutions of species II (M = W): $W(CO)_5DPF$ in PC + 0.1 M TEAP showed a singlet at δ -50.3 ppm (with satellites corresponding to coupling $^{31}P-^{183}W$) ascribed to the phosphorus atom linked to the tungsten atom in $W(CO)_5DPF$ (II, M = W). A second singlet was observed at δ -68.3 ppm attributed to the phosphorus atom not bonded to $W(CO)_5$. After exhaustive electrolysis of II: $W(CO)_5DPF$ at -1.8 V/SCE (first reduction step, Table 2), i.e. after consumption of 1 F per mole, the solution turned red and its ^{31}P NMR spectrum revealed that free DPF (characterized by the ^{31}P resonance signal at δ -72.4 ppm [4] was the predominant phosphorus containing species in the solution. On the other hand, when a solution of III: $[W(CO)_5]_2DPF$ was exhaustively reduced at -1.8 V (two first reduction steps, Table 2), i.e. after consumption of 2 F per mole, the same observation was made. This solution turned red, and its ^{31}P NMR spectrum gave a signal at δ -72.4 ppm, characteristic of free DPF in solution.
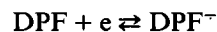
As the two first reduction steps of III (M = W) were too close together to allow exhaustive coulometric reduction corresponding to the first electron transfer, the above coupling of electrolysis with ^{31}P NMR spectroscopy could not be used to determine whether or not one P–M bond had already been broken after the first electron was added to III. To ascertain whether the reduction scheme of III (first two reductions) was electrochemical-electrochemical-chemical (EEC) or ECEC, cyclic voltammetry was carried out on III at $+20°C$, $0°C$, $-10°C$ and $-20°C$, respectively. The results indicate that the relative magnitudes of the first two reduction peaks remained unchanged over this temperature range. The third reduction peak current, corresponding to the reduction of fragment I liberated by chemical reaction following the second electron transfer, decreased as expected from $+20$ to $-20°C$ with respect to the peak current corresponding to the first reduction. Thus, as it is unlikely that the rupture of identical P–M bonds could be extremely fast after the first electron transfer and much slower after the second, the reduction mechanism of III is probably EEC on the time scale of cyclic voltammetry, and the first two electrochemical steps (EE) each involves one of the $M(CO)_5$ moities.

We propose the following reduction mechanism for complexes II and III (M = W):
Type II species: $W(CO)_5DPF$

(a) First reduction step

$$W(CO)_5 + e \rightarrow [W(CO)_5DPF]^-$$

$$[W(CO)_5DPF]^- \xrightarrow{chem} W(CO)_5^- + DPF$$
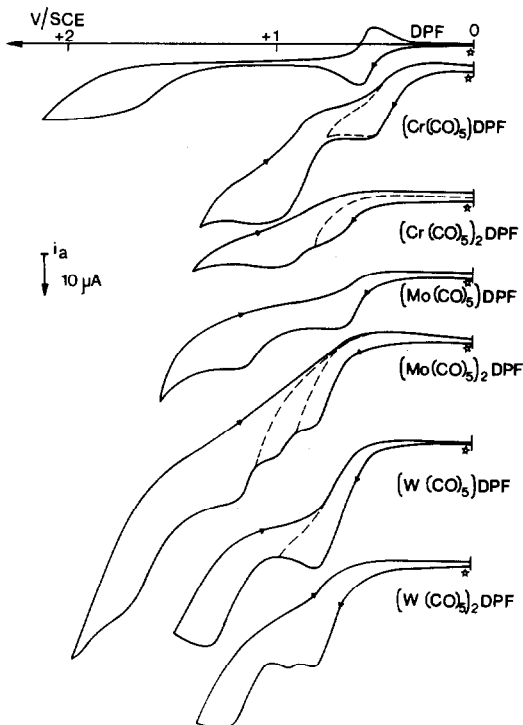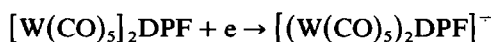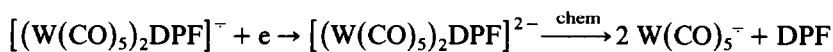
(b) Second reduction step

$$DPF + e \rightleftharpoons DPF^-$$

Fig. 2. Oxidation of DPF, $[M(CO)_5]DPF$, $[M(CO)_5]_2DPF$ with M = Cr, Mo, W. Cyclic voltammetry on a platinum electrode (3.14 mm^2) in propylene carbonate containing 0.1 M TEAP, v 0.05 V/s, $c \simeq 5 \times 10^{-4}$ M. *Start of the scan.

Type III species: $[W(CO)_5]_2DPF$

(a) First reduction step

$$[W(CO)_5]_2DPF + e \rightarrow [(W(CO)_5)_2DPF]^-$$

(b) Second reduction step

$$[(W(CO)_5)_2DPF]^- + e \rightarrow [(W(CO)_5)_2DPF]^{2-} \xrightarrow{\text{chem}} 2 \ W(CO)_5^- + DPF$$

(c) Third reduction step

$$DPF + e \rightleftarrows DPF^-$$
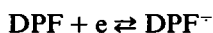
On mercury electrodes the oxidation potential of I is shifted anodically from $+0.53$ V to $\sim +0.70$ vs. SCE by the presence of one $M(CO)_5$ in complex II. The oxidation potentials of complexes III were not accessible under our experimental conditions on mercury electrodes.

Oxidation of the complexes on a Pt electrode

Compound I undergoes a reversible one-electron oxidation at $E_{1/2}$ 0.57 V vs. SCE, whereas the complexes II and III show several irreversible oxidations in the potential range 0 to $+1.5$ V vs. SCE (Table 2 and Fig. 2).

In order to avoid electrode passivation, which was observed in rotating disc electrode voltammetry, cyclic voltammetry was used. In propylene carbonate con-
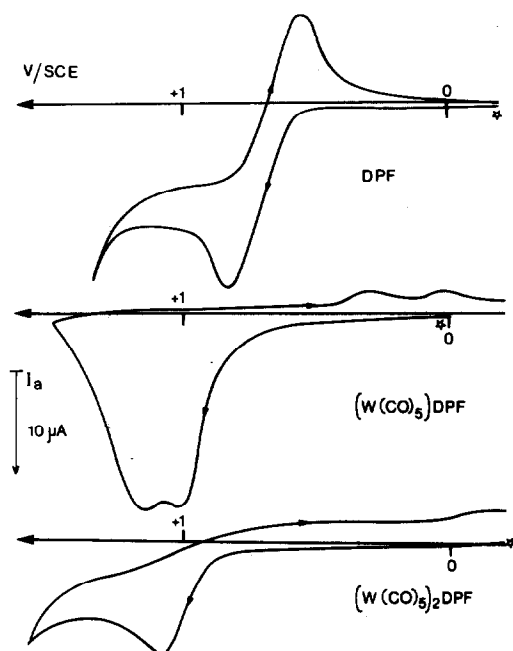
Fig. 3. Cyclic voltammetric curves (oxidation) for DPF, $[W(CO)_5]DPF$, $[W(CO)_5]_2DPF$ in CH_2Cl_2 containing 0.1 $M(C_6H_{13})_4N^+ ClO_4^-$ on a platinum electrode, $v = 0.1$ V/s, $c \simeq 5 \times 10^{-4}$ M. *Start of the scan.

taining 0.1 M TEAP, complexes II undergo two irreversible oxidation steps with peak currents having the same value, whereas complexes III show several ill-defined oxidation steps with unequal peak currents. We attribute the first oxidation of complexes II and III to the oxidation of the fragment I on the basis of the value of the peak potentials and the fact that this oxidation becomes reversible at high potential scan rates (beyond 1 V/s). The second oxidation step of compounds II can therefore be attributed to the oxidation of $M(CO)_5$-containing moieties, and the potential values follow the sequence, Cr (+1.00 V) < Mo (+1.15 V) < W (+1.25 V). In complexes II and III the complete analysis of the characteristics of these oxidation steps was prevented by passivation of the electrode even after the first oxidation step. The chemical reactions responsible for this passivation clearly involve the solvent, even though they are of low donicity, as is evident for both propylene carbonate and CH_2Cl_2 (Fig. 2 and 3). As electrooxidation of either $W(CO)_6$ or $W(CO)_5(CH_3CN)$ does not result in passivation of the platinum electrode, we therefore attribute the passivation to a strong interaction of the oxidized ligand I with the electrode. On the return scan of cyclic voltammograms a reduction peak appears near 0 V vs. SCE which involves a decomposition product of I^+ as previously observed in the oxidation of I^1.

Discussion

Free DPF(I) in solution shows a reversible one-electron oxidation (on Pt electrode) and a reversible one-electron reduction at potentials more anodic than the

corresponding potentials for ferrocene. The phosphorus atoms have a greater influence on the energy of the LUMO than on the energy of the HOMO in I, as indicated by the relative magnitudes of the observed reduction and oxidation potential shifts for I compared to ferrocene. This is consistent with recent quantum mechanical calculations [8] which show the LUMO to have ~ 33% phosphorus character whereas the HOMO has only ~ 4% phosphorus character in $(\eta\text{-}C_4H_4P)_2Fe$ complex. Furthermore, both free and coordinated cations I^+ are less stable than the ferrocinium cation [1,7].

Oxidation

Coordination of I through its phosphorus atom to a $M(CO)_5$ (M = Cr, Mo, W) group to give complexes II generally renders I more difficult to oxidize (Table 2). This qualitatively confirms that coordination of $M(CO)_5$ to I decreases the overall electron density on I. This oxidation potential is only slightly affected by the nature of the metal M, and follows the sequence W (+ 0.76 V) > Mo (0.65 V) > Cr (0.55 V) < I (0.57 V). Although the variation is small, it is as large as the change in the oxidation potentials observed within the $M(CO)_6$ series (Table 1). The variation of these potentials with M can be rationalized by taking into account the increase in the acceptor properties of $M(CO)_5$ in the order Cr < Mo < W. The ligand I acts overall as an electron donor, but this effect is small, in accord with the good π-acceptor and fairly poor σ-donor character of I. This is supported by the Graham parameters [11], is $\Delta\sigma = -0.27$ and $\Delta\pi = 0.52$ for II (M = Mo) [4].

Reduction

The reductive electron transfer around -1.8 V/SCE for complexes II and III is associated with the $P\text{-}M(CO)_5$ moiety (M = Cr, Mo, W). If the first reduction potentials of species II or the second potentials of species III are compared with those of $M(CO)_6$ and $M(CO)_5PC$ (PC = propylene carbonate) [5,6b], it is clear that replacement of one CO ligand by DPF (I) in $M(CO)_6$ significantly facilitates the reduction, by 0.50 V (Cr) > 0.32 V (Mo) > 0.28 V (W). Finally, the last reduction step in II and III is the reduction of DPF (I). The slight difference observed between the reduction potential of free DPF (I) (-2.33 V) and the values measured in studying the reduction II and III arises from the chemical reaction preceding this reduction (cf. reaction scheme).

The first reduction steps in species II and III, associated with the $P\text{-}M(CO)_5$ moieties, occur at less cathodic potentials (Table 2), than those of the corresponding $M(CO)_6$ complexes (Table 1).

Similarly, the second oxidation step in species II and III, involving the $P\text{-}M(CO)_5$ moieties, occur at less anodic potentials than those of the corresponding $M(CO)_6$ complexes. Thus these potential shifts cannot be rationalized in terms of σ donor/π acceptor properties alone, although such effects are present together with the effects of the irreversibility of the electrochemical step and of the occurrence of chemical reactions. Rather, the facilitated reduction and oxidation in species II and III if compared to $M(CO)_6$ must be ascribed to changes in the molecular orbitals energies from $M(CO)_6$ to $M(CO)_5L$ (L = monodentate ligand other than CO), as consistently predicted [10] from shifts and lower degeneracy of HOMO and LUMO levels in $M(CO)_5L$. On the other hand these results clearly reveal the lack of cooperativity between metallic centers in II and in III, as well as the fact that the central iron

provides an effective barrier to the transmission of substituent effects from one phospholyl ring to the other.

Experimental

The compounds, I, II and III were prepared and purified as previously described [4], and handled under argon. Electrochemical measurements were performed, as previously described [1], under argon in solvent freshly distilled under argon. Phosphorus chemical shifts are relative to external 85% H_3PO_4 (δ positive for downfield shifts) and were obtained on a spectrometer Bruker SY 200, for propylene carbonate solution containing 0.1 M TEAP containing $CDCl_3$ as internal lock.

Acknowledgments

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