

## Photoreduction of Carbon Dioxide to Carbon Monoxide with Hydrogen Catalyzed by a Rhenium(I) Phenanthroline–Polyoxometalate Hybrid Complex

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**Abstract:** A phenanthroline ligand decorated at the 5,6-position with a 15-crown-5 ether was used to prepare a metalorganic–polyoxometalate hybrid complex  $\text{Re}^{\text{I}}(\text{L})(\text{CO})_3\text{CH}_3\text{CN}-\text{MHPW}_{12}\text{O}_{40}$  ( $\text{L} = 15\text{-crown-5-phenanthroline}$ ,  $\text{M} = \text{Na}^+$ ,  $\text{H}_3\text{O}^+$ ). X-ray diffraction,  $^1\text{H}$  and  $^{13}\text{C}$  NMR, ESI-MS, IR, and elemental analysis were used to characterize this complex. In the presence of Pt/C, the polyoxometalate moiety in  $\text{Re}^{\text{I}}(\text{L})(\text{CO})_3\text{CH}_3\text{CN}-\text{MHPW}_{12}\text{O}_{40}$  can oxidize  $\text{H}_2$  to two protons and two electrons which in the presence of visible light can catalyze the photoreduction of  $\text{CO}_2$  to CO with  $\text{H}_2$  as the reducing agent instead of the universally used amines as sacrificial reducing agents. An EPR spectrum of a stable intermediate species under reaction conditions shows characteristics of a  $\text{PW}^{\text{VI}}\text{W}^{\text{VI}}_{11}\text{O}_{40}$  and a  $\text{Re}^0$  species with a tentative assignment of the intermediate as  $\text{Re}^0(\text{L})(\text{CO})_3(\text{S})-\text{MH}_3\text{PW}^{\text{VI}}\text{W}^{\text{VI}}_{11}\text{O}_{40}$ .

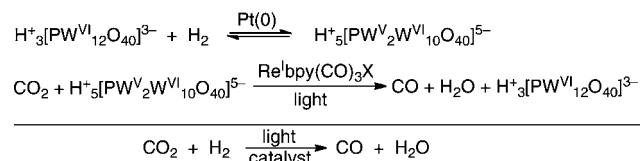
The extensive use of fossil fuels over the past century has likely led to a significant increase in the amount of  $\text{CO}_2$  in the atmosphere and has mandated intensive efforts for the realization of alternative energy resources.<sup>1</sup> A great deal of this effort is directed to the utilization of solar energy. One enticing topic in this broad endeavor is the solar photoreduction of  $\text{CO}_2$  to various higher energy products so as to store solar energy as chemical energy and create renewable fuels.<sup>2</sup> Since one-electron reduction of  $\text{CO}_2$  to  $\text{CO}_2^{\cdot-}$  is energetically highly unfavorable, the energetically more favorable pathway is to use proton assisted multiple-electron transfer that can be realized with visible light. A common motif in this area is to utilize a transition-metal coordination compound as a photocatalyst. Examples of photocatalysts that require a photosensitizer are cobalt and nickel tetraaza-macrocycles,<sup>3</sup> while iron and cobalt porphyrins and similar unsaturated macrocycles<sup>4</sup> and rhenium bipyridine complexes<sup>5</sup> do not require photosensitizers. Enzyme catalysts have also recently been described for such photoreductions.<sup>6</sup> A very significant drawback in the utilization of these photocatalysts has been that sacrificial reducing agents, typically trialkylamines and trialkanolamines, are essential for the photoreduction reaction.<sup>7,8</sup> Therefore, an important goal would be to replace these sacrificial reducing agents with a more renewable resource.

Since the earlier reports by Lehn and co-workers<sup>5a,b</sup> on the use of  $[\text{Re}^{\text{I}}(\text{L})(\text{CO})_3\text{X}]$  ( $\text{X} = \text{Cl}, \text{Br}$ ; and  $\text{L} = \text{bipyridine}, \text{phenanthroline}$ ) as photocatalysts in solution for selective reduction of  $\text{CO}_2$  to CO, such Re(I) complexes are being extensively investigated although there is apparently still no consensus on the mechanism of formation of CO.<sup>5d</sup> Upon irradiation,  $[\text{Re}^{\text{I}}(\text{bipy})(\text{CO})_3\text{X}]$  is promoted to a triplet metal-to-ligand charge transfer ( $^3\text{MLCT}$ ) excited state which

is reductively quenched by a sacrificial tertiary amine electron donor to yield the catalytically active  $[\text{Re}^{\text{I}}(\text{bpy}^{\cdot-})(\text{CO})_3\text{S}]^-$ .<sup>9</sup> The next steps are thought to involve formation of a  $\text{Re}-\text{CO}_2$  adduct and protonation leading to a rhenium metalcarboxylic acid intermediate. Further reduction requires an additional electron and proton to yield CO and  $\text{H}_2\text{O}$ . Binuclear rhenium intermediates have also been proposed to explain the reduction of the metalcarboxylic acid intermediate.<sup>5g,h</sup>

The objective of this research was to replace amine sacrificial donors by hydrogen ( $\text{H}_2$ ) in the  $[\text{Re}^{\text{I}}(\text{L})(\text{CO})_3\text{X}]$  photocatalyzed reduction of  $\text{CO}_2$  to CO and  $\text{H}_2\text{O}$ . Analysis of the mechanistic information available as very briefly summarized above suggests that  $\text{H}_2$  could be utilized for such reactions if oxidized to two protons and two electrons. In fact it is known from the literature that polyoxometalates can oxidize  $\text{H}_2$  in such a way especially in the presence of Pt(0).<sup>10</sup> The concept of replacing the sacrificial tertiary amine reducing agent by  $\text{H}_2$  is summarized in Scheme 1.

### Scheme 1. Proposed Photoreduction of $\text{CO}_2$ with $\text{H}_2$



In this context it is notable that the reaction in its entirety is a reverse water gas shift reaction; however, at ambient temperature the reaction is thermodynamically *very unfavorable*;  $\Delta G_r$  (25 °C) = 6.81 kcal/mol ( $K_{\text{eq}} = 9.7 \times 10^{-6}$ ).<sup>11</sup> A photochemical transformation at 298 K is, therefore, a viable alternative.

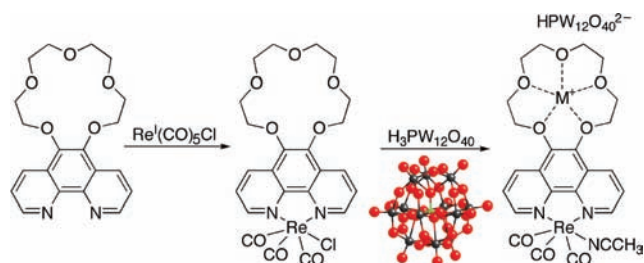
It has also been shown in the past that polyoxometalates can be combined with coordination compounds to form metalorganic–polyoxometalate hybrid complexes with advantageous catalytic activity.<sup>12</sup> Relevant to this research is the possibility of preparing 1,10-phenanthroline decorated at the 5,6-position with a 15-crown-5 ether group so that the phenanthroline moiety can be used to prepare the needed Re(I) complex and the crown ether group is available for complexation of Keggin-type polyoxometalates.<sup>13</sup> This leads to the formation of a  $\text{Re}^{\text{I}}(\text{L})(\text{CO})_3(\text{CH}_3\text{CN})-\text{MHPW}_{12}\text{O}_{40}$  compound where  $\text{L} = 5,6\text{-}(15\text{-crown-5})\text{-}1,10\text{-phenanthroline}$ ,  $\text{M} = \text{H}_3\text{O}^+$ ,  $\text{Na}^+$ , Scheme 2.

Mixing acetonitrile solutions of  $\text{Re}^{\text{I}}(\text{L})(\text{CO})_3\text{Cl}$  and  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  followed by slow evaporation of the solvent led to the formation of  $\text{Re}^{\text{I}}(\text{L})(\text{CO})_3(\text{CH}_3\text{CN})-\text{MHPW}_{12}\text{O}_{40}$ . The IR spectrum (see Supporting Information, SI) showed that both of the component parts were indeed present as expected. The ESI-MS of  $\text{Re}^{\text{I}}(\text{L})(\text{CO})_3(\text{CH}_3\text{CN})-\text{MHPW}_{12}\text{O}_{40}$  dissolved in aqueous methanol in the positive ion mode showed a cluster of peaks at  $m/z = 682.04$  attributable to a  $\text{Re}^{\text{I}}(\text{L})(\text{CO})_3(\text{CH}_3\text{CN})$  fragment, while the ESI-

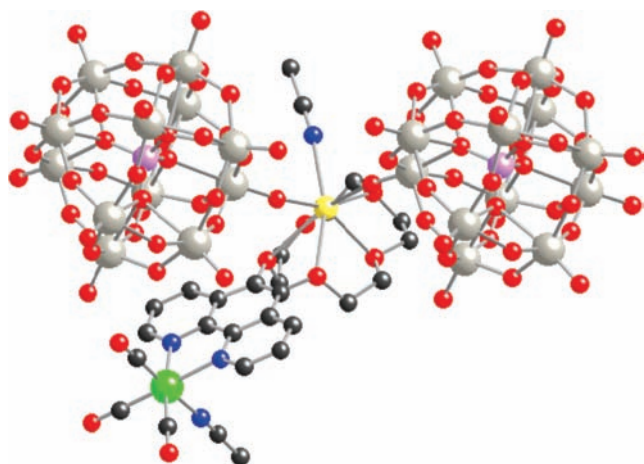
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**Scheme 2.** Preparation of  $\text{Re}^{\text{I}}(\text{L})(\text{CO})_3(\text{CH}_3\text{CN})\text{-MHPW}_{12}\text{O}_{40}$  (W, black; P, green; O, red)



MS (SI) in the negative ion mode showed a major cluster of peaks centered at  $m/z = 959$  attributable to the  $[\text{PW}_{12}\text{O}_{40}]^{3-}$  ( $z = 3$ ) fragment. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR in  $\text{CD}_3\text{CN}$  and  $\text{CD}_3\text{CON}(\text{CD}_3)_2$  (SI) supports the formulation of the  $\text{Re}^{\text{I}}(\text{L})(\text{CO})_3(\text{solvent})$  fragment. Finally, we were able to crystallize  $\text{Re}^{\text{I}}(\text{L})(\text{CO})_3(\text{CH}_3\text{CN})\text{-MHPW}_{12}\text{O}_{40}$ ;<sup>14</sup> an X-ray structure is presented in Figure 1. The



**Figure 1.** Ball and stick structure of  $\text{Re}^{\text{I}}(\text{L})(\text{CO})_3(\text{CH}_3\text{CN})_2\text{-NaHPW}_{12}\text{O}_{40} \cdot 3\text{CH}_3\text{CN} \cdot 3.5\text{H}_2\text{O}$  showing the complexation of two  $\text{PW}_{12}\text{O}_{40}$  units to Na. H atoms and solvent molecules are not shown. C, black; N, blue; O, red; P, purple; Na, yellow; Re, green; W, gray.

more notable features of the structure are that (1) each crown ether moiety complexes a sodium cation, which is in turn binding two  $\text{PW}_{12}\text{O}_{40}$  moieties, (2) the complexation of two polyoxometalates to each Na atom lengthens the Na–O bonds (up to 2.94 Å) which is compensated by  $\text{CH}_3\text{CN}$  as a ligand to Na, and (3) the hybrid complex forms a 1D polymer (Figure S1).

In order to carry out the photocatalytic studies 0.5  $\mu\text{mol}$  of  $\text{Re}^{\text{I}}(\text{L})(\text{CO})_3(\text{CH}_3\text{CN})\text{-MHPW}_{12}\text{O}_{40}$  was dissolved in 0.5 mL of dimethylacetamide (DMA)<sup>15</sup> in a 5 mL Pyrex pressure tube with a filter allowing light transmission at  $\geq 380$  nm;  $\sim 20$   $\mu\text{g}$  of 5% Pt/C was added, the mixture was purged and then brought to 1 bar with 99.99%  $\text{CO}_2$ , and then an additional 2 bar of  $\text{H}_2$  was added. The magnetically stirred suspension was irradiated at room temperature with a 150 W xenon lamp for 14 h.

Analysis of the gas phase of the reaction mixture by GC-TCD showed the average formation of 11.3  $\mu\text{mol}$  of CO (22.6 turnovers, quantum yield 0.011) and a small amount of  $\text{CH}_4$  (0.5  $\mu\text{mol}$ , 1.0 turnover), Table 1, entry 1. Analysis of the liquid phase by GC-FID and GC-MS did not detect the formation of additional products such as  $\text{CH}_3\text{OH}$ ,  $\text{CH}_2\text{O}$ , or  $\text{HCOOH}$ . A similar reaction using 5% Pt/ $\text{Al}_2\text{O}_3$  in place of Pt/C was less efficient yielding only 2.7  $\mu\text{mol}$  of CO (5.4 turnovers), Table 1, entry 2. Various control reactions were carried out to verify that the CO formed indeed was from  $\text{CO}_2$  and not the DMA solvent or catalyst (entries 3 and 4).

**Table 1.** Photoreduction of  $\text{CO}_2$  Catalyzed by  $\text{Re}^{\text{I}}(\text{L})(\text{CO})_3(\text{CH}_3\text{CN})\text{-MHPW}_{12}\text{O}_{40}$  Using  $\text{H}_2$ <sup>a</sup>

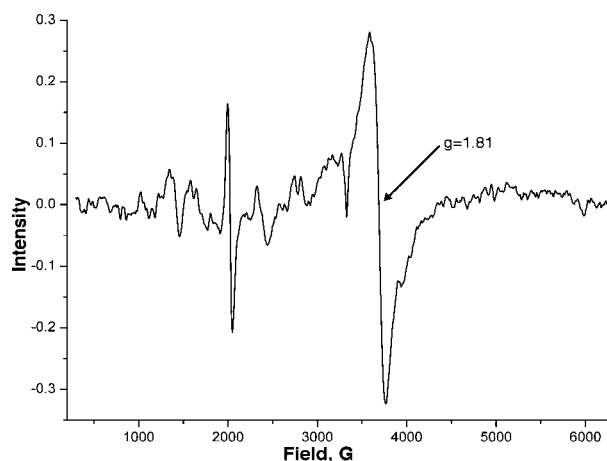
Catalyst	$\text{CO}$ , $\mu\text{mol}$	Comments
1 $\text{Re}^{\text{I}}(\text{L})(\text{CO})_3(\text{CH}_3\text{CN})\text{-MHPW}_{12}\text{O}_{40}$	11.3 <sup>b</sup>	
2 $\text{Re}^{\text{I}}(\text{L})(\text{CO})_3(\text{CH}_3\text{CN})\text{-MHPW}_{12}\text{O}_{40}$	5.4	Pt/ $\text{Al}_2\text{O}_3$
3 $\text{Re}^{\text{I}}(\text{L})(\text{CO})_3(\text{CH}_3\text{CN})\text{-MHPW}_{12}\text{O}_{40}$	ND	No $\text{CO}_2$
4 $\text{Re}^{\text{I}}(\text{L})(\text{CO})_3(\text{CH}_3\text{CN})\text{-MHPW}_{12}\text{O}_{40}$	ND	No $\text{CO}_2$ , no $\text{H}_2$
5 $\text{Re}^{\text{I}}(\text{L})(\text{CO})_3(\text{CH}_3\text{CN})\text{-MHPW}_{12}\text{O}_{40}$	ND	No Pt/C
6 $\text{Re}^{\text{I}}(\text{L})(\text{CO})_3(\text{CH}_3\text{CN})$	ND	
7 $\text{H}_3\text{PW}_{12}\text{O}_{40}$	ND	
8 $\text{Re}^{\text{I}}(\text{L})(\text{CO})_3(\text{CH}_3\text{CN})\text{-MHPW}_{12}\text{O}_{40}$	ND	No light
9 $\text{Re}^{\text{I}}(\text{phenanthroline})(\text{CO})_3(\text{Cl})$ and $\text{H}_3\text{PW}_{12}\text{O}_{40}$	ND	

<sup>a</sup> Reaction conditions: catalyst (0.5  $\mu\text{mol}$ ), DMA (0.5 mL), 20  $\mu\text{g}$  Pt/C,  $\text{CO}_2$  (1 bar),  $\text{H}_2$  (2 bar), 20 °C, 14 h under irradiation with a 150 W Xe lamp. ND: not detected. Analysis of products for gaseous products ( $\text{CO}$ ,  $\text{CO}_2$ , and  $\text{CH}_4$ ) was by GC-TCD using a Carbonplot capillary column. No products were detected in analysis of the liquid phase by GC-FID and GC-MS using a 5% phenylmethylsilicone capillary column.

<sup>b</sup> Average of five runs.

Additional control reactions verified that all the reaction components were needed for  $\text{CO}_2$  reduction to CO (entries 5–8). Interestingly, a combination of a *nondecorated* complex and polyoxometalate,  $\text{Re}^{\text{I}}(\text{phenanthroline})(\text{CO})_3(\text{Cl})\text{-H}_3\text{PW}_{12}\text{O}_{40}$ , (entry 9), did not yield detectable amounts of reduction products.

We were interested in obtaining some mechanistic insight into the possible reaction mechanism for  $\text{CO}_2$  reduction. In reactions catalyzed by  $\text{Re}^{\text{I}}(\text{bipy})(\text{CO})_3\text{X}$  with sacrificial tertiary amine donors, it has been proposed<sup>5d</sup> that the catalyst is photoactivated to the  $^3\text{MLCT}$  excited state and then reduced by  $\text{R}_3\text{N}$  to yield the radical anion,  $\text{Re}^{\text{I}}(\text{bipy}^{\cdot-})(\text{CO})_3\text{X}$ . This key intermediate is then suggested to react with  $\text{CO}_2$  in a mono- or bimolecular mechanism, eventually leading to formation of CO. As hypothesized in Scheme 1,  $[\text{PW}_{12}\text{O}_{40}]^{3-}$  alone did react with  $\text{H}_2$  in the presence of Pt(0) to yield a typical heteropoly blue with a  $\lambda_{\text{max}}$  at 656 nm. This sample was also EPR silent at 130 K as expected for singlet (antiferromagnetically coupled spins)  $[\text{PW}^{\text{V}}_2\text{W}^{\text{VI}}_1\text{O}_{40}]^{5-}$ . On the other hand  $\text{Re}^{\text{I}}(\text{L})(\text{CO})_3(\text{CH}_3\text{CN})\text{-MHPW}_{12}\text{O}_{40}$  reacted in the presence of all the reaction components to yield a paramagnetic species. An X-band EPR spectrum at 130 K showed a complex spectrum, Figure 2.



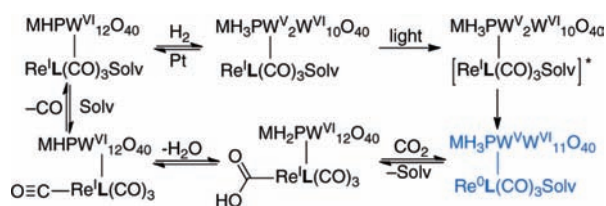
**Figure 2.** X-band EPR at 130 K of  $\text{Re}^{\text{I}}(\text{L})(\text{CO})_3(\text{CH}_3\text{CN})\text{-MHPW}_{12}\text{O}_{40}$  after exposure to typical reaction conditions (see footnote, Table 1). Microwave frequency, 9.36 GHz; microwave power, 20 mW; field modulation, 1 G; time constant, 1.3 s; scan time, 163.84 s.

There are two main features: a peak at  $g = 1.81$  attributable to a isotropic spectrum of a doublet  $[\text{PW}^{\text{V}}\text{W}^{\text{VI}}_1\text{O}_{40}]^{4-}$  fragment as described in the literature<sup>16</sup> and a very broad anisotropic spectrum of a  $\text{Re}^0$  fragment.<sup>17</sup> Most importantly, a ligand centered radical

anion,  $g = 2.00$ , with a narrow peak width (50–100 G) was *definitively* not observed.<sup>18</sup> The visible spectra (SI) of a  $\text{Re}^0$  compound<sup>17</sup> and reduced polyoxometalate overlap and thus were not mechanistically informative; in the near-UV a peak at 325 nm after reaction is attributable to the reduced polyoxometalate as this peak is also observed when reacting  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  alone. The IR peaks for CO shifted to lower wavenumbers, 2004 and  $1877\text{ cm}^{-1}$  due to the higher charge density on Re, Figure S8.

From the results obtained one can assume that the slowly formed intermediate whose EPR spectrum is presented above is a stable species that reacted with  $\text{CO}_2$  and led to its reduction. Therefore, a working hypothesis for the reduction of  $\text{CO}_2$  to CO may be postulated, Scheme 3.  $\text{H}_2$  is activated by Pt and is oxidized to two

**Scheme 3.** A Possible Pathway for the Photoreduction of  $\text{CO}_2$  with  $\text{H}_2$  to CO and  $\text{H}_2\text{O}$  with a  $\text{Re}^I(\text{L})(\text{CO})_3(\text{CH}_3\text{CN})\text{-MHPW}_{12}\text{O}_{40}$  Catalyst



electrons and two protons and  $\text{Re}^I(\text{L})(\text{CO})_3(\text{S})$  is photoactivated to the  $^3\text{MLCT}$  excited state by visible light.<sup>19</sup> Together these processes yield a  $\text{Re}^0(\text{L})(\text{CO})_3(\text{S})\text{-MH}_3\text{PW}^V\text{W}^VI_{10}\text{O}_{40}$  species (blue in Scheme 3), likely by intramolecular electron transfer since only the hybrid compound is reactive (compare Table 1, entries 1 and 9), which is so tentatively assigned by its EPR spectrum. The remaining relatively fast reaction steps that were not observed are based on a monomolecular mechanism in the literature.<sup>5d</sup>

Although the turnover frequency and quantum yield observed in the present reduction of  $\text{CO}_2$  with  $\text{H}_2$  is lower than has been reported for previous rhenium catalyzed photoreductions of  $\text{CO}_2$  with amines,<sup>5,20</sup> we feel that the use of  $\text{H}_2$  in such systems represents an advance. Furthermore, the hybrid complex enables  $\text{CO}_2$  reduction with  $\text{H}_2$  using visible light as opposed to other semiconductor catalysts, e.g.  $\text{Ga}_2\text{O}_3$ ,  $\text{MgO}$ , or  $\text{TiO}_2$ , that require UV irradiation.<sup>21</sup> The concept of oxidation of  $\text{H}_2$  by polyoxometalates and storage of the resulting electrons and protons on the polyoxometalate may also prove useful in a myriad of other photoreduction reactions that presently use amines as sacrificial reducing agents.

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**Supporting Information Available:** Full experimental details and additional spectra and characterizations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (14) In fact two types of crystals grew, but the second type was too fragile to remove from solution. It is enticing to assign the second crystals as having an  $\text{H}_3\text{O}^+$  cation instead of  $\text{Na}^+$  since the latter was not added and probably scavenged from the solutions/glassware.
- (15) DMF is often used as a solvent in  $\text{Re}^I(\text{bipy})(\text{CO})_3(\text{X})$  catalyzed photoreductions of  $\text{CO}_2$  with tertiary amines; DMA gave better results.
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- (19) Note that although  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  is also a known photocatalyst. (Hiskia, A.; Mylonas, A.; Papaconstantinou, E. *Chem. Soc. Rev.* **2001**, *30*, 62–69) it is only excited by UV light.
- (20) It is known that  $\text{H}_2\text{O}$  slows the reaction and its presence (the catalyst is a hydrate) may be a reason for less turnover.
- (21) (a) Teramura, K.; Tsuneoka, H.; Shishido, T.; Tanaka, T. *Chem. Phys. Lett.* **2008**, *467*, 191–194. (b) Kohno, Y.; Ishikawa, H.; Tanaka, T.; Funabiki, T.; Yoshida, S. *Phys. Chem. Chem. Phys.* **2001**, *3*, 1108–1114. (c) Lo, C.-C.; Hung, C.-H.; Yuan, C.-S.; Wu, J.-F. *Solar Energy Mater. Solar Cells* **2007**, *91*, 1765–1774.

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