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Chemical switching behaviour of tricarbonylrhenium(I) complexes of a new redox active 'Pincer' ligand

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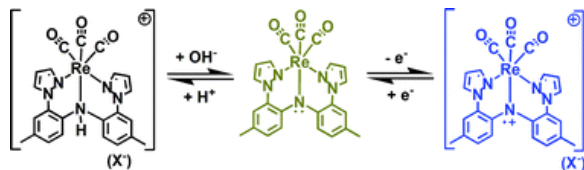
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Abstract

The structures and optoelectronic properties of tricarbonylrhenium(I) complexes of di(2-pyrazolyl-*p*-tolyl)amine in its neutral and deprotonated (uninegative amido) form were investigated. Reactions of the complexes with Brønsted acids or bases result in distinctive changes of colour and electrochemical activity owing to the non-innocent nature of the ligand.



Introduction

Simple chemical species that can be dependably switched between multiple, easily-distinguishable (readable), electronic states by external stimuli and that retain their integrity without the need for permanent stimulation are highly desirable for information storage applications in the emerging area of molecular electronics.¹ Numerous organic systems such as diarylethenes, flavylum derivatives, among other more complex examples have been recognized or developed for such purposes.² Recently, there has been growing interest in developing similar chemistry for organometallic systems owing to the attractive electronic properties associated with metal centres such as access to multiple oxidation states, different spin states, intense charge transfer absorptions, and large spin-orbit coupling constants that can potentially give rise to interesting photophysical properties.³

During the course of our investigations into the coordination chemistry of new pincer ligands⁴ (typically meridionally-coordinating and uninegative species) based on di(2-pyrazolyl-aryl)amine derivatives (left, Fig. 1), it occurred to us that a few of these complexes might be viable entrants for switching purposes and possibly for information storage applications owing to their interesting optoelectronic properties and chemical reactivity. That is, as diarylamines are well-known electron-donors,⁵ pincer ligands based on this scaffold are electrochemically non-innocent;⁶ they will increase the number of available valence states in their transition metal complexes. Moreover, since the electron donor capacity of these ligands relies on nitrogen being coordinatively unsaturated (with a lone pair of electrons), it should be possible to attenuate energetic access to electronic states involving this lone pair (such as any $n-\pi^*$ or $d\pi-\rho\pi$ interaction) *via* quarterization (binding protons or other Lewis acids). Our choice of using pyrazolyl donors is based on the facile syntheses of nearly limitless structural variants that can be exploited to impart control over steric, electronic, and solubility properties (by changing pyrazolyl Rgroups in Fig. 1). During the course of these studies an important contribution was reported by Ozerov, Nocera, and co-workers⁷ regarding a related complex *mer*-(PNP)Re^I(CO)₃ (**A**) (R = *i*Pr; X = Me, right of Fig. 1). The yellow complex **A** was found to react with triflic acid to produce the colorless {*mer*-[H(PNP)]Re(CO)₃}(OTf) (**B**) with a protonated nitrogen. Additionally, oxidation of **A** with AgOTf afforded royal blue {*mer*-[(PNP)]Re(CO)₃}(OTf) (**A⁺OTf⁻**). The IR, EPR spectroscopic data and chemical reactivity of **A⁺OTf⁻** were indicative of a ligand-centred radical (with relatively weak coupling to the metal centre). The potential switching behaviour of **A** (or **B**), however, was not addressed despite the interesting colour changes and reversible redox properties.

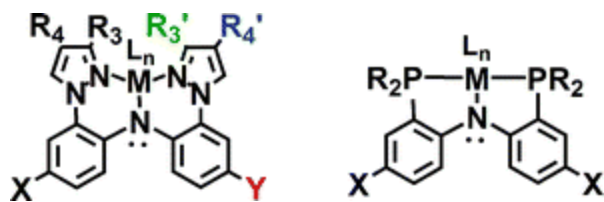


Fig. 1 Generic depiction of a metal complex of a NNN ‘pincer’ ligand based on di(2-pyrazolyl-aryl)amine and of a related PNP derivative.

In this communication we highlight our initial findings concerning the properties and potential switching behaviour of the $\text{Re}(\text{CO})_3$ complexes of di(2-pyrazolyl-*p*-tolyl)amine, **HL**, ($R_3 = R_3' = R_4 = R_4' = \text{H}$; $X = Y = \text{CH}_3$, [Fig. 1](#)). Importantly, this study also allows a comparison of the impact of changing donor groups at the 2,2'-positions on the diarylamine on the electronic properties of resultant (NNN) $\text{Re}^I(\text{CO})_3$ or (PNP) $\text{Re}^I(\text{CO})_3$ complexes. Future reports will more fully detail the chemistry promoted uniquely by complexes of this ligand type (and substituted derivatives) as well as comparisons with the remarkable known chemistry exhibited by related PNP derivatives.[8](#)

As detailed in the Electronic Supplementary Information (ESI[†]), the pincer ligand **HL** is prepared in two steps from commercially-available di(*p*-tolyl)amine by first *ortho*-bromination with elemental bromine to give (2-Br-*p*-tolyl)₂NH.[9](#) Subsequently, a CuI-catalyzed amination reaction of the latter with pyrazole gives the desired ligand in 70% yield.[10](#) The amination reaction appears to occur stepwise, as small amounts of (2-pz-*p*-tolyl)(2-Br-*p*-tolyl)NH can be isolated from incomplete reactions. As anticipated, **HL** is an electron donor giving an irreversible oxidation ($i_{pc}/i_{pa} \sim 0.6$; $\Delta E \sim 490$ mV) at about 0.59 V *versus* Fc/Fc⁺ in CH_2Cl_2 . The syntheses and structures of the various *fac*- ReCO_3 complexes is partly summarized in [Fig. 2](#) and expanded upon in the ESI. [†]The colourless toluene-insoluble *fac*- $\text{ReBr}(\text{CO})_3[\kappa^2\text{N}(\text{HL})]$ (**1**) is obtained in high yield by the reaction between the ligand and $\text{Re}(\text{CO})_5\text{Br}$ in toluene. In **1**, the ligand binds rhenium in a *cis*-chelating fashion through two of the three nitrogen donors, one from a pyrazolyl arm and the other from the sp^3 -amino nitrogen, giving a pseudo-octahedral ReBrC_3N_2 kernel. Reaction of **1** with TI ($X = \text{PF}_6$ or OTf) in CH_3CN affords high yields of very pale yellow {*fac*- $\text{Re}(\text{CO})_3[\kappa^3\text{N}(\text{HL})]$ }(X) (**2·X** or simply **2**) where the ligand is facially-bound to rhenium with all three of its available nitrogen donors. Reaction of either **1** or **2·PF₆** with one equivalent of $(\text{NEt}_4)(\text{OH})$ in CH_3CN immediately causes elimination of H_2O and $(\text{NEt}_4)(\text{Br}$ or $\text{PF}_6)$ to produce bright yellow *fac*- $\text{Re}(\text{CO})_3[\kappa^3\text{N}(\text{L})]$ (**3**) with a nearly planar central amido nitrogen ($\Sigma\angle$'s about N1 = 356°). It is noted that the low thermal stability of the lithium salt **LIL** (dec. > -15 °C) precluded the direct synthesis of **3** from $\text{Re}(\text{CO})_5\text{Br}$, similar to the preparation of the related PNP complex **A**. It is re-emphasized that in contrast to the PNP derivatives which possess *mer*- ReCO_3 cores, the complexes of **HL** have only exhibited *fac*- ReCO_3 moieties regardless of the synthetic route. As such, the three C–O stretches of each **1–3** ([Table 1](#)) are consistent with the low symmetry of the complexes and the average stretching frequencies decrease in the order **2** > **1** > **3** in accord with expectations based on the increasing electron density at metal centres (and greater back-bonding). Interestingly, the IR data (KBr) for **2** and those reported for **B** are nearly identical despite the very different donor sets and the data for **A** are more consistent with those of **1** than those of **3**. These observations can be reconciled by considering the *trans*-influence of different groups in the *fac*- *versus* *mer*-complexes.

Table 1 IR and electrochemical data for various $\text{Re}(\text{CO})_3$ complexes

Compound	$\nu_{\text{C-O}}$ cm^{-1} ^{a,c}	$E_{1/2}$ (V vs. Fc/Fc ⁺) ^b
1	2021, 1919, 1882; avg 1941	<i>irr.</i> $E_{pa} = +1.07, +0.67, +0.23$
2	2042, 1952, 1928; avg. 1974	<i>irr.</i> $E_{pa} = +1.17$
3	2013, 1901, 1876; avg. 1930	0.00
A_c	2026, 1909, 1891; avg. 1942	-0.25
B_c	2048, 1943, 1928; avg. 1973	<i>irr.</i> $E_{pa} = +0.93$

- KBr pellet.
- CH_2Cl_2 (**1–3**) or CH_3CN (**A & B**), 100 mV s^{-1} , TBAH.
- Ref. [7](#)

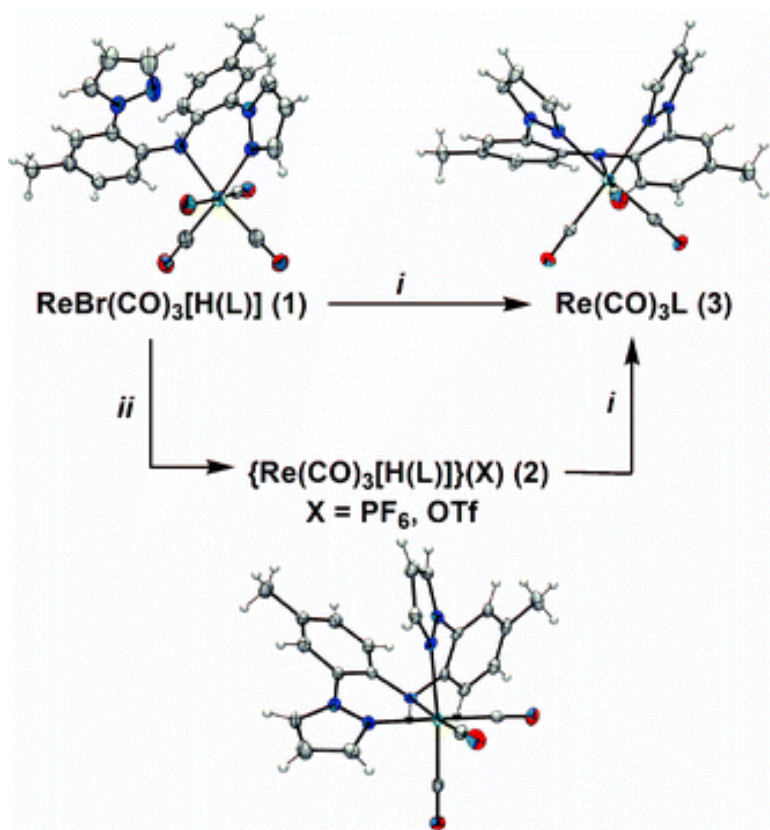


Fig. 2 Syntheses and structures of *fac*- Re(CO)_3 complexes (ORTEP Ellipsoids drawn at 50% probability). Anion removed from **2**· PF_6 for clarity. Key: *i*. 1 eq. $(\text{NEt}_4)(\text{OH})$ in MeOH, CH_3CN , 15 min (69%); *ii*. $\text{Ti}(\text{PF}_6$ or $\text{OTf})$, CH_3CN , 12 h (80%).

Similar to the electrochemistry reported for PNP complexes **A** and **B**, that of **3** is distinct from its protonated derivatives **2**· PF_6 or **1** (Table 1). Complex **3** shows a quasi-reversible oxidation¹¹ in CH_2Cl_2 at 0.00 V versus Fc/Fc^+ ($i_{\text{pc}}/i_{\text{pa}} = 1$, but $\Delta E = E_{\text{pa}} - E_{\text{pc}}$ increases as a function of scan rate) whereas the other two complexes have irreversible oxidations ($i_{\text{pc}}/i_{\text{pa}} \ll 1$ and $\Delta E \gg 59$ mV) at higher potentials. These ligand-based oxidations in **A** or **B** are understandably more favourable than those in **3** and **2** given the relative inductive effects of PR_2 versus pyrazolyl groups on the diarylamine backbone.

As detailed in the ESI † one-electron oxidation of **3** with AgOTf or organic oxidants forms blue-green $(\mathbf{3}^+)(\text{X})$ ($\text{X} = \text{OTf}$ or SbCl_6) that appear stable as solids but very slowly decompose ($t_{1/2} = 3$ d) at 295 K in CH_2Cl_2 or CH_3CN . Unfortunately, it has not been possible to obtain X-ray quality crystals of $(\mathbf{3}^+)(\text{X})$. As with $\mathbf{A}^+\text{OTf}^-$, the IR, and EPR spectroscopic data along with DFT calculations (UB3LYP/LACVP*) of $(\mathbf{3}^+)$ indicate a ligand-centred radical. The shift in average ν_{CO} only increases by 41 cm^{-1} on traversing between **3** and $\mathbf{3}^+$ similar to the 38 cm^{-1} increase for the PNP derivatives⁷ but less than the $50\text{--}100 \text{ cm}^{-1}$ found for metal-centred oxidations.¹² The X-band (9.65 GHz) EPR spectra (Fig. 3) at 293 K shows a well-resolved sextet signal centred at $g_{\text{iso}} = 2.0177$ with $a_{\text{iso}} = 4.95(7)$ mT due to the hyperfine interaction between the electronic spin and the $^{185/187}\text{Re}$ nuclei ($I = 5/2$). At 10 K the spectrum is pseudo-rhombic and can be adequately simulated with $g_{x,y,z} = 2.020, 2.020, 2.005$ and $a_{x,y,z}^{\text{Re}} = 4.0, 5.2, 4.0$ mT with inclusion of a small quadrupole interaction $P = 0.3$ mT, $\epsilon = 0.1$ mT. The relatively small deviation of g -values from that for the free electron $g_e = 2.0023$ and small hyperfine coupling are in line with a ligand- rather than a metal-centred radical.^{7,13} These observations are also consistent with theoretical calculations that indicate most of the spin density is located on the ligand.

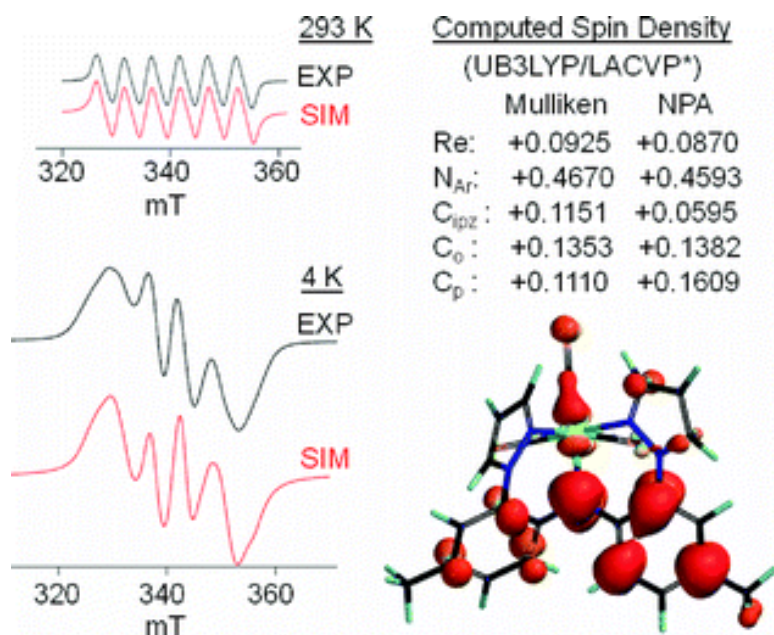


Fig. 3 Left: X-Band (9.63 GHz) EPR spectra (3^+)(SbCl_6) in CH_2Cl_2 at 293 K (top) and 10 K (bottom); Right: Spin density map from DFT calculations (UB3LYP/LACVP*).

The significant differences in the optical spectra of $2\cdot\text{X}$, 3 , and 3^+ (Fig. 4) and the electrochemical activity of these species prompted further investigation into their potential chemical switching behaviour mediated by Brønsted acids and bases. Thus, the interconversions between $2\cdot\text{X}$ and 3 using $\text{H}(\text{BF}_4)$ and $(\text{NEt}_4)(\text{OH})$ were monitored by both electronic absorption and voltammetric experiments (Fig. 5). While these initial titration experiments showed the viability of performing switching operations, the reversibility over multiple reaction cycles was variable, being dependent upon the concentration mandated by the analytical technique being employed (10^{-5}m for UV, 10^{-4}m for CV). The more concentrated samples afforded higher reversibility as indicated by the quantity of acid or base required to achieve the maximum signal intensity indicative of 3 . Currently the origin of the signal degradation is not clear and is the subject of ongoing investigations in our laboratory.

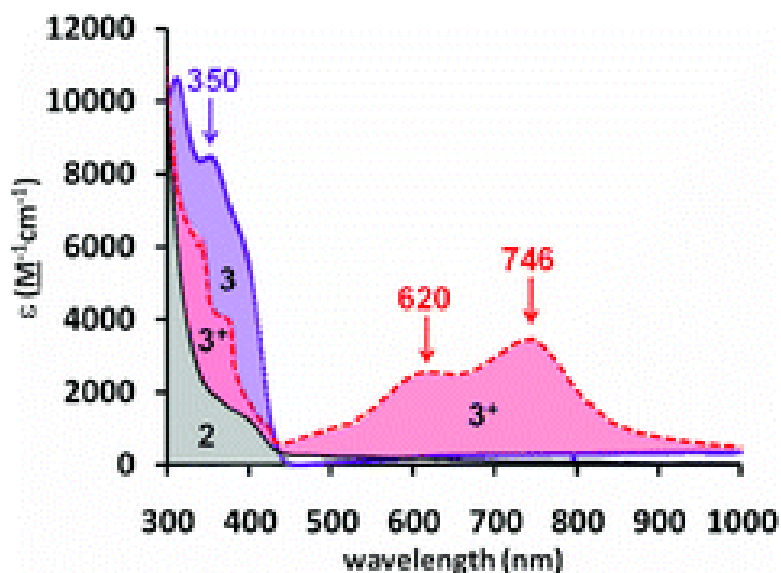


Fig. 4 Overlay of absorption spectra of $2\cdot\text{PF}_6$ (grey), 3 (violet), and 3^+)(SbCl_6) (red) in CH_2Cl_2 .

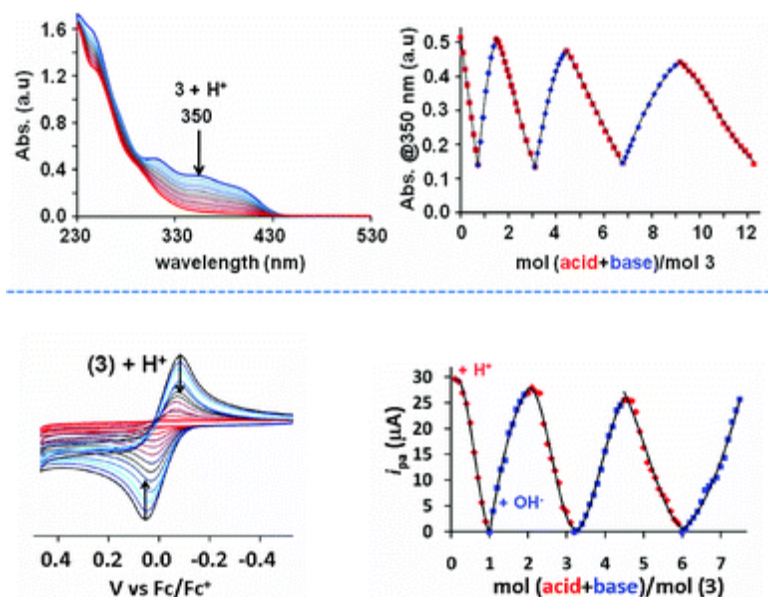


Fig. 5 UV-Vis spectral (top) and voltammetric (bottom, 100 mV s^{-1}) changes attendant upon titration of CH_2Cl_2 solutions of **3** first with a methanolic solution of HBF_4 and then with $(\text{NEt}_4)(\text{OH})$ in MeOH to *in situ* generated **2**. A minimum of three cycles are shown for each.

Conclusions

The optical and electrochemical properties of tricarbonylrhenium(i) complexes of a new electroactive NNN-tridentate ligand can be gated by reactions with Brønsted acids or bases which serve to modulate energetic access to the lone pair of electrons on the central nitrogen that govern the electrochemical activity and associated electronic ($n-\pi^*$ or $d\pi-p\pi$) transitions. It is hoped that appropriate modifications of the ligand on either the pyrazolyls or the diarylamine portion will address the current issues of small signal losses observed during cycling reactions. From this perspective, the PNP ligands or PNN hybrids of [Fig. 1](#) may also offer some advantages for $\text{Re}(\text{CO})_3$ -based systems that should be examined.

References

1. *Molecular Nanoelectronics*, M. A. Reed and T. Lee, American Scientific Publishers, Stevenson Ranch, CA, 2003, T. Mrozek, J. Daub and A. Ajayaghosh, *Molecular Switches*, B. L. Feringa Wiley-VCH, New York, 2001,
2. V. Balzani, A. Credi and M. Venturi, *Molecular Devices and Machines: Concepts and Perspectives for the Nanoworld, 2nd Ed.*, Wiley-VCH, Weinheim, 2008,
3. C. Olivier, B. Kim, D. Touchard and S. Rigaut, *Organometallics*, 2008, **27**, 509. D.-H. Chae, J. F. Berry, S. Jung, F. A. Cotton, C. A. Murillo and Z. Yao, *Nano Lett.*, 2006, **6**, 165. B. Yin, F. Niemeyer, J. A. G. Williams, J. Jiang, A. Boucekine, L. Toupet, H. Le Bozec and V. Guerchais, *Inorg. Chem.*, 2006, **45**, 8584 E. Evangelio and D. Ruiz-Molina, *Eur. J. Inorg. Chem.*, 2005, 2957
4. O. V. Ozerov *The Chemistry of Pincer Compounds*, D. Morales-Morales and C. M. Jensen, Elsevier, New York, 2007,
5. For instance, A. Rajca, M. Vale and S. Rajca, *J. Am. Chem. Soc.*, 2008, **130**, 9099
6. D. Adhikari, S. Mossin, F. Basuli, J. C. Huffman, R. K. Szilagyi, K. Mayer and D. J. Mindiola, *J. Am. Chem. Soc.*, 2008, **130**, 3676 S. B. Harkins and J. C. Peters, *Inorg. Chem.*, 2006, **45**, 4316. S. B. Harkins and J. C. Peters, *J. Am. Chem. Soc.*, 2005, **127**, 2030. S. B. Harkins and J. C. Peters, *J. Am. Chem. Soc.*, 2004, **126**, 2885
- a. T. Radosevich, J. G. Melnick, S. A. Stoian, D. Bacciu, C.-H. Chen, B. M. Foxman, O. V. Ozerov and D. G. Nocera, *Inorg. Chem.*, 2009, **48**, 9214

7. J. I. von der Vlugt and J. N. H. Reek , *Angew. Chem., Int. Ed.*, 2009, **48** , 8832 .and references
8. L. Fan , B. M. Foxman and O. V. Ozerov , *Organometallics*, 2004, **23** , 326.
9. T. J. Morin , S. V. Lindeman and J. R. Gardinier , *Eur. J. Inorg. Chem.*, 2009, 104 B. J. Liddle , R. M. Silva , T. J. Morin , F. P. Macedo , R. Shukla , S. V. Lindeman and J. R. Gardinier , *J. Org. Chem.*, 2007, **72** , 5637.and references
10. See ESI† for more details. The quasi-reversible nature of the wave (and scan rate dependence) is retained in other solvents (CH₃CN, THF) and is likely a result of slow structural reorganization on the time-scale of the cyclic voltammetry experiment, as will be detailed in the full paper
11. D. Chong , D. R. Laws , A. Nafady , P. J. Costa , A. L. Rheingold , M. J. Calhorda and W. E. Geiger , *J. Am. Chem. Soc.*, 2008, **130** , 2692. F. A. Cotton , K. R. Dunbar , L. R. Falvello and R. A. Walton , *Inorg. Chem.*, 1985, **24** , 4180.
12. Compare also to: L. A. DeLearie , R. C. Haltiwanger and C. G. Pierpont , *Inorg. Chem.*, 1989, **28** , 644

Footnote

† Electronic supplementary information (ESI) available: Experimental procedures, crystal data, and other characterization data. CCDC reference numbers [759658–759662](#). For ESI and crystallographic data in CIF or other electronic format see DOI: [10.1039/c001344g](#)