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Frustrated Lewis pair chemistry of CO

Douglas W. Stephan [ab]

Transition metal species readily capture and react with CO as the metal can act both as an acceptor and donor of electron density. In contrast, such a situation is less common in the main group and thus far fewer examples of main group CO adducts and their subsequent reactivity have been studied. In this review, we focus on the application of the concept of Frustrated Lewis Pairs (FLPs) to develop main group chemistry of CO. Specifically, we address reactions of FLPs that illustrate the ability to capture CO in addition to subsequent reactivity involving reduction with a variety of reagents. These developments illustrate that the donation and acceptance of electron density provided by FLPs is an alternative strategy to advance the reactivity of CO. Such insights augur well for future advances in the homogeneous chemistry of CO.

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Chair for Chemical Society Reviews and is now Chair of the editorial board of Chemical Communications. A world-leading researcher in inorganic chemistry/catalysis, he is best known as the founder of the field of "frustrated Lewis pair" (FLP) chemistry. He has received several National and International awards, including Humboldt and Killam Fellowships. He is a Fellow of the Royal Society (London), a Corresponding Member of North-Rhein-Westfaelia Academy of the Sciences and Arts and was an Einstein Visiting Fellow at TU Berlin. More recently, he was the recipient of the 2019 J. C. Polanyi Award from NSERC of Canada, a 2020 Guggenheim Fellowship the 2021 Killam Prize in Science, a 2021 Centenary Prize and the 2022 F. A Cotton Award from the ACS.

1. Introduction

Carbon monoxide (CO) is a common ligand in organometallic complexes. As a quintessential example of a "non-classic" ligand, it interacts with a metal centre *via* σ-donation and acts as a π-acceptor by accepting metal d-orbital electron density into its π*-orbitals. This back-donation from the metal strengthens the metal–carbon bond accounting for the ability of metal to form carbonyl derivatives.

In contrast, the interactions of CO with boron derivatives are much less common as these Lewis acidic species can accept donation from CO, but do not have low lying d-electrons available for back donation. Consequently, it is only derivatives that offer very high Lewis acidity that are capable of forming isolable CO adducts. For example, as early as 1937, the species $H_3B(CO)$ was described (Fig. 1).[1] In 2002, the species $(F_3C)_3B(CO)$ was prepared and crystallographically characterized (Fig. 1).[2] Subsequently, in 2014 Erker and co-workers showed that Piers' borane $[HB(C_6F_5)_2]$ forms an adduct with CO (Fig. 1).[3] More recently, the
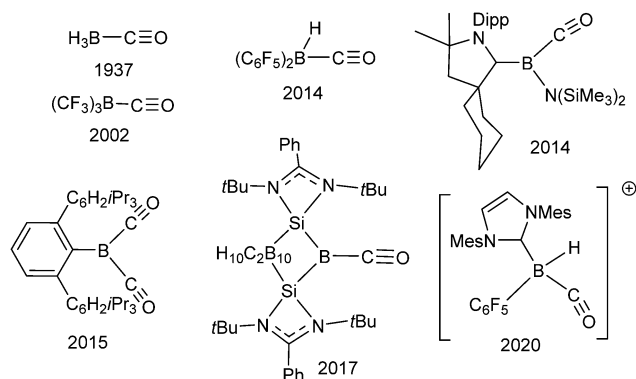

Fig. 1   Examples of Boron adducts of CO.

Erker group reported the use of a highly Lewis acidic cation to capture CO, affording the adduct $[(IMes)BH(C_6F_5)(CO)]^+$ (Fig. 1).[4] Another more recent strategy has been to employ reduced B-species. Several such borylene species have been shown to capture CO (Fig. 1).[5–7]

Concurrent with these efforts, the field of frustrated Lewis pair (FLP) chemistry has emerged.[8–14] This concept exploits combinations of donor and acceptor molecules to affect the activation of small molecules. While the initial findings were focused on dihydrogen activation[15,16] and inferred that steric inhibition of adduct formation was essential, these views have also evolved. Indeed, FLP chemistry has been applied to the activation of wide range of small molecules including alkynes, olefins, CO_2, N_2O, SO_2, SO, cyclopropanes, among others finding applications in organic synthesis, polymer chemistry and heterogeneous catalysis.[8–14] Moreover, explorations of the nature of FLPs have broadened our understanding regarding both the mode of action and the range of Lewis acids and bases that can act as FLPs.

The long history of transition metals binding and activation of CO by acting as both an electron acceptor and donor, prompted questions about similar activation by the combined action of Lewis acids and bases. This notion together with the demonstrated ability of FLPs to effect catalytic metal-free hydrogenation, further prompted speculation of the possibility of transition metal-free mimics of classical Fischer–Tropsch chemistry.

In this review, we discuss the recent developments in the FLP chemistry of CO. We begin by first describing conventional B/P FLP systems that capture CO (Section 2). This is followed by a discussion of stoichiometric reduction reactivity of CO with p-block FLPs (Section 3) and transition metal-based FLPs (Section 4). Stoichiometric reactivity of alkali metal-based FLPs providing synthetic routes to isocyanides and the homologation and reduction of CO are discussed (Section 5). The use of heterogeneous FLP systems in catalytic CO reduction is also presented (Section 6). We conclude with a discussion of the general lessons and a consideration of the future prospects for further development.

2. CO capture

The concept of using FLPs to capture CO is predicated on the notion that the donor and acceptor requirements, typically seen for CO binding to a transition metal do not need to reside on a single atom, but rather can be provided by separated donor and acceptor molecules. In this fashion, the potential for reduction chemistry of CO can be further expanded employing main group species.
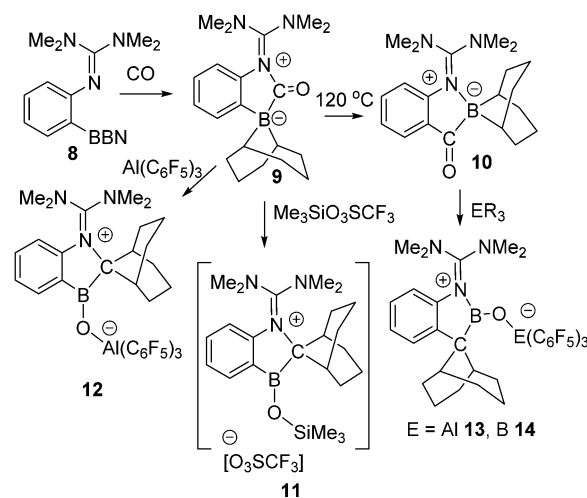
The demonstration of the ability of FLPs to capture CO was first described in 2010 for the boron-amidinate, $HC(iPrN)_2-B(C_6F_5)_2$ **1** (Scheme 1).[17] Although the ring-opened amidinate (*i.e.* the FLP) was not spectroscopically observed, it is believed that transient separation of a donor nitrogen of the amidinate and the acceptor boron atom act in concert to capture CO to give $HC(iPrN)_2(CO)B(C_6F_5)_2$ **2** (Scheme 1). A much more recent paper[18] has reported a related system based on the ferrocene
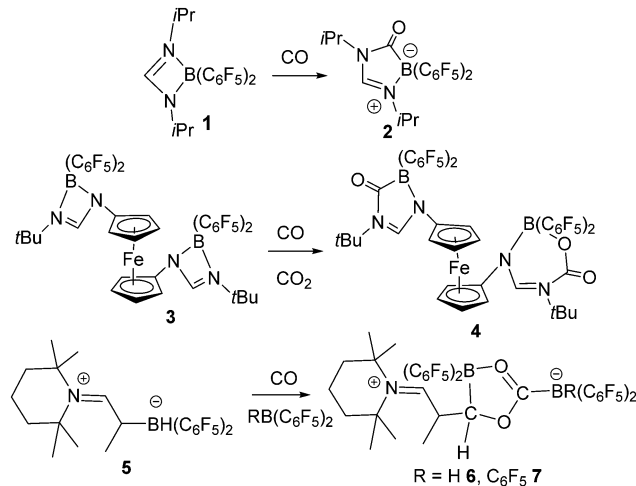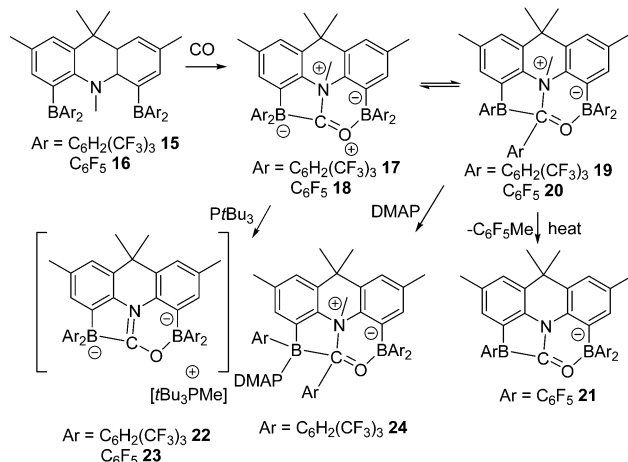

Scheme 1 CO capture by a B/N species.

linked bis-boron amidinate $(tBuN=CHN(9-BBN)C_5H_4)_2Fe$. This species was shown to concurrently capture two molecules of CO while the related $(tBuNCHN(B(C_6F_5)_2)C_5H_4)_2Fe$ **3** was able to capture CO_2 and CO simultaneously to generate $(tBuNCHNC-(O)(B(C_6F_5)_2)$ $C_5H_4)(tBuNCHNCO_2(B(C_6F_5)_2)C_5H_4)Fe$ **4** (Scheme 1). In a related fashion in 2017,[19] the Erker group described the reaction of the B/N zwitterion $C_5H_6Me_4N=CHC(Me)HB(H)(C_6F_5)_2$ **5** with CO in the presences of $HB(C_6F_5)_2$ or $B(C_6F_5)_3$. Interestingly, in these cases CO-insertion into the B–H bond and C–O coupling affords products of the form $C_5H_6Me_4N=CHC(Me)C(B(C_6F_5)_2)(H)OC(O)(B(C_6F_5)_2R)$ (R = H **6**, C_6F_5 **7**) (Scheme 1).

More recently, a 2021 report from Krempner and coworkers[20] described the remarkable reaction of the B/N FLP $C_6H_4(9-BBN)(N=C(NMe_2)_2)$ **8** with CO. While at room temperature this species captures CO to give **9**, at 120 °C the B and CO fragment swap places affording $C_6H_4C(O)(9-BBN)(N=C(NMe_2)_2)$ **10** (Scheme 2). In contrast, in the presence of $Me_3SiO_3SCF_3$ a further rearrangement occurs to give $C_6H_4B(OSiMe_3)(CC_8H_{14})(N=C(NMe_2)_2)$ **11**. Similarly in the presence of $Al(C_6F_5)_3$,

Scheme 2 CO capture and subsequent reactions using the Krempner FLP.

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Chem. Soc. Rev., 2023, **52**, 4632–4643 | **4633**

Scheme 3 The subsequent reactivity following CO capture by a B$_2$N FLP.

$C_6H_4B(OAl(C_6F_5)_3)(CC_8H_{14})(N=C(NMe_2)_2)$ **12** was obtained. In a related fashion the species **9** also reacts with electrophiles to induce B/C rearrangement, affording $C_6H_4(CC_8H_{14})BO(E(C_6F_5)_3)$ $(N=C(NMe_2)_2)$ (E = Al **13**, B **14**) (Scheme 2).

Also in 2021, Aldridge and coworkers[21] described the interaction of the NB$_2$ species, $(Ar_2BC_6H_2Me)_2(CMe_2)NMe$ (Ar = $C_6H_2(CF_3)_3$ **15**, C_6F_5 **16**) with CO. At room temperature, these species captured CO to give **17/18**, respectively. Reversible arene migrations from B to the carbonyl carbon generated **19** and **20** (Scheme 3). On warming, C_6F_5Me is lost with the formation of CO bridge between the two B atoms with a B–N bond formation $(Ar_2BC_6H_2Me)(CMe_2)NCO-BAr(C_6H_2Me)$ (Ar = C_6F_5 **21**) (Scheme 3). In the additional presence of PtBu$_3$, the methyl bound to N is transferred to phosphorus affording the phosphonium salts $[t$Bu$_3$PMe] $[(Ar_2BC_6H_2Me)_2$ $(CMe_2)NCO]$ (Ar = $C_6H_2(CF_3)_3$ **22**, C_6F_5 **23**) (Scheme 3). In contrast, addition of DMAP (DMAP = $Me_2NC_5H_4N$) afforded coordination of the pyridyl nitrogen to give a four-coordinate boron centre of **19**, affording $(DMAP)(ArBC_6H_2Me)(CMe_2)NC(Ar)OBAr(C_6H_2Me)$ (Ar = $C_6H_2(CF_3)_3$ **24**). Most notably, the tuning of the boron substituents in **15** permitted the initially colourless species to capture CO in the temperature range of 40–70 °C with a dramatic colour change to red upon formation of **17** and **19**. This provides a colorimetric test for gaseous CO.

2.1 Insights

The early examples described above demonstrate the notion of CO capture by group 13/15 FLP combinations of Lewis acids and bases. In addition, Aldridge and coworkers[21] have exploited such FLP capture of CO towards a sensor technology. While the concept of FLP based sensors is an intriguing one, the findings set the stage for the reactivity studies targeting chemistry of FLP sequestered CO.

3. p-Block FLPs and reactivity of CO

Given the established ability of FLPs to capture CO, the next obvious questions are around the notions of reactivity and the potential for reduction. Of course, the wide variety of inter- and
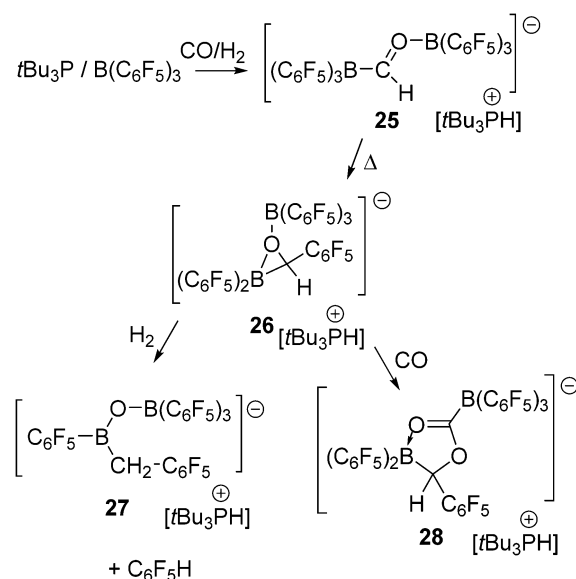
intramolecular FLPs that are accessible provide a broad chemical landscape to address this question. Below, the reactivity of a number of conventional main group FLP systems with CO are discussed.
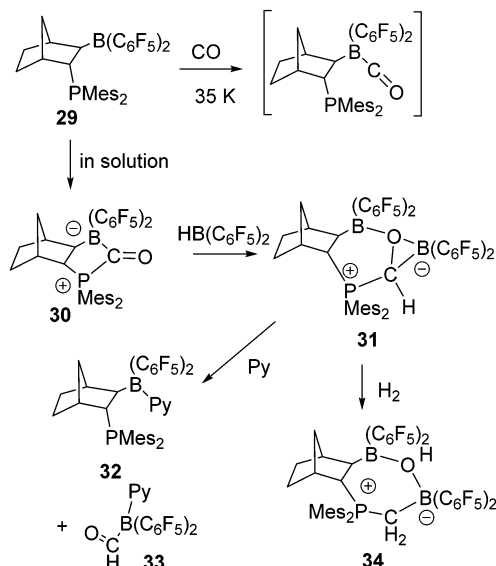
3.1 Intermolecular P/B FLPs

In a 2013 study,[22] we explored the reactivity of the FLP tBu$_3$P/ $B(C_6F_5)_3$ with syn-gas (CO/H$_2$). This afforded the salt $[t$Bu$_3$PH]- $[(C_6F_5)_3BC(H)OB(C_6F_5)_3]$ **25** (Scheme 4). Warming this species induced the migration of C_6F_5 to the formyl-carbon atom, effecting the reduction of the C=O bond and affording the salt $[t$Bu$_3$PH]- $[(C_6F_5)_2BC(H)(C_6F_5)OB(C_6F_5)_3]$ **26** (Scheme 4). This species reacted with H$_2$ inducing the elimination of C_6F_5H, and the cleavage of the C–O bond affording the formation of salt of the anion $[C_6F_5B-(CH_2C_6F_5)OB(C_6F_5)_3]^-$ **27**. On the other hand, **26** also reacted with additional CO effecting ring-expansion of the formyl-borane fragment affording the rare alkylcarboxylato-borate anion $[(C_6F_5)_2-BC(H)(C_6F_5)OCOB(C_6F_5)_3]^-$ **28** (Scheme 4).

3.2 Intramolecular P/B FLPs

Concurrent with the above studies, examination of the use of P/B intramolecular FLPs in reactions with CO were undertaken by the Erker group. This work began with the report of the exposure of P/B FLP $Mes_2PC_7H_{10}B(C_6F_5)_2$ **29** to CO (Scheme 5). In an argon matrix at 10 K, no reaction was observed. However, on warming to *ca.* 35 K the borane-CO adduct was observed as evidenced by the IR stretching frequency at 2196 cm^{-1}. This is somewhat higher in wavenumbers than that observed for free CO.[23] Reactions of **29** with CO in solution afforded the FLP/CO addition product $Mes_2PC_7H_{10}B(C_6F_5)_2(CO)$ **30** (Scheme 5), which was only stable below 240 K. In this species binding of B/P to CO affords a trigonal planar geometry at C, while the CO stretching frequency was 1791 cm^{-1}. In **30**, as in the FLP adducts **2** and **4**, the CO fragment acts both as a σ-donor and a π-acceptor. However, in contrast to the Dewar–Chatt–

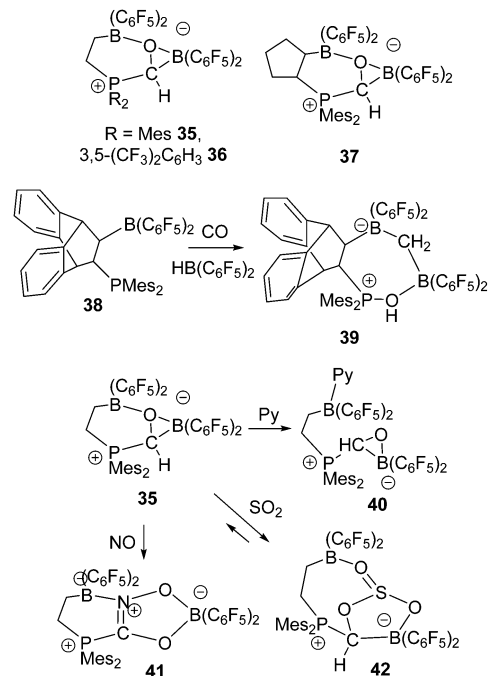**Scheme 4** Reactivity of intermolecular B/P FLP with syn-gas.

4634 | Chem. Soc. Rev., 2023, **52**, 4632–4643

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Scheme 5   CO capture and reduction by intramolecular FLPs.

Scheme 6   Structures and reactions of η^2-formyl-borane FLP species.

Duncanson model[24,25] for the interactions of transition metals with CO, the acceptor and donor sites are disparate being on the B and P sites, respectively.

In a subsequent effort, Erker et al.[26] showed that the CO fragment in the FLP-CO adduct **29** was reduced via a net hydroboration in the presence of $(C_6F_5)_2BH$ yielding the epoxy-borate species, $Mes_2PC_7H_{10}B(C_6F_5)_2(\mu\text{-HCO})B(C_6F_5)_2)$ **31** (Scheme 5). In a further study,[27] the Erker group showed that treatment of **31** with pyridine generated the pyridine adduct of **29**, **32** and the formyl-borane-pyridine adduct $HC(O)B(C_6F_5)_2(Py)$ **33**. In this same report,[27] the "η^2-formyl-borane" species **31** was reduced by H_2 (60 bar) at 25 °C to yield C–O bond cleavage affording $Mes_2P(CH_2)C_7H_{10}B(C_6F_5)_2(\mu\text{-OH})B(C_6F_5)_2$ **34** (Scheme 5). The activation of H_2 in this case is thought to result from the dissociation of the formyl-borane from the borane centre in **31**. This generates a B/O FLP capable of heterolytic cleavage of H_2 while subsequent hydride transfer from boron to carbon affords **34** (Scheme 5). In a related sense, borane/ether combinations were subsequently shown to be active for catalytic FLP hydrogenations of olefins.[28]
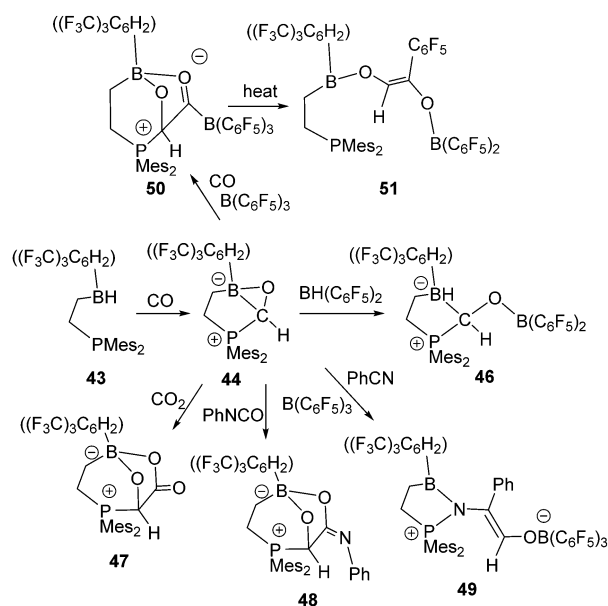
Analogous η^2-formyl-borane species were also obtained from the FLPs, $Mes_2PCH_2CH_2B(C_6F_5)_2$[26] (3,5-$(CF_3)_2C_6H_3)_2$-$PCH_2CH_2B(C_6F_5)_2$[29] and $Mes_2PC_5H_8B(C_6F_5)_2$[26,30] affording the formyl borane-derivatives **35–37**, respectively (Scheme 6). The analogous chemistry with a "semi-triptycene" back-bone FLP $(C_6H_4CHCH_2)_2PMes_2B(C_6F_5)_2$ **38** in reaction with CO gave $(C_6H_4CHCH_2)_2PMes_2(CH_2)B(C_6F_5)_2(\mu\text{-OH})B(C_6F_5)_2$ **39** (Scheme 6).[31] In contrast, the formyl borane adduct Mes_2PCH_2-$CH_2B(C_6F_5)_2(\mu\text{-HCO})B(C_6F_5)_2$ **35** reacted with pyridine to generate the borane-pyridine adduct $(py)B(C_6F_5)_2CH_2CH_2PMes_2$$(\mu\text{-HCO})B(C_6F_5)_2$ **40** (Scheme 6). In a further study,[32] **35** reacted with NO to effect C–N coupling with loss of a hydrogen radical generating HNO and the product $Mes_2PCH_2CH_2B(C_6F_5)_2$$(\mu\text{-(O)C}=\text{NO})B(C_6F_5)_2$ **41** (Scheme 6). In a related fashion **35** also reacted with SO_2 effecting insertion into the formylborato-

ring to give $Mes_2PCH_2CH_2B(C_6F_5)_2(\mu\text{-HC}(B(C_6F_5)_2)OSO_2)$ **42** (Scheme 6).[33] This capture of SO_2 was subsequently shown to be reversible.[34]

3.3   Secondary intramolecular P/B FLPs

The Erker group explored the inclusion of secondary B fragments in FLPs. The species $Mes_2PCH_2CH_2B(H)(C_6H_2(CF_3)_3)$ **43**[35] reacted with CO, undergoing insertion into the B–H bond afforded the borato-epoxide species $Mes_2PCH_2CH_2B(\mu\text{-HC(O)})(C_6H_2(CF_3)_3)$ **44** (Scheme 7). The analogous CO addition product Mes_2PCH=

Scheme 7   Reactions of BH-derived FLPs with CO.

C(SiMe$_3$)B(μ-HC(O))(C$_6$H$_2$(CF$_3$)$_3$) **45** was also reported.[36] Species **44** was also shown to further react with HB(C$_6$F$_5$)$_2$ to give Mes$_2$PCH$_2$CH$_2$B(H)(μ-HC(OB(C$_6$F$_5$)$_2$)) (C$_6$H$_2$(CF$_3$)$_3$) **46** (Scheme 7). In a further subsequent study,[37] compound **44** also reacted with CO$_2$, isocyanate, and nitrile in the presence of B(C$_6$F$_5$)$_3$ to effect C–C coupling reactions to give **47–49**, respectively. Similarly, **44** in the presence of CO and B(C$_6$F$_5$)$_3$ also effect C–C coupling to generate **50** which upon heating affords the enolate derivative **51** (Scheme 7).

In a similar fashion, the FLP incorporating secondary phosphine fragment was also probed.[38] The reaction of the FLP (tBu$_3$C$_6$H$_2$)P(H)CH$_2$CH$_2$B(C$_6$F$_5$)$_2$ **52** (Scheme 8) with CO and HB(C$_6$F$_5$)$_2$ gave (tBu$_3$C$_6$H$_2$)P(H)CH$_2$CH$_2$B(C$_6$F$_5$)(CH(B(C$_6$F$_5$)$_3$)O) **53**. Subsequent addition of this zwitterion with pyridine gave coordination to boron and induced C$_6$F$_5$ transfer affording (tBu$_3$C$_6$H$_2$)P(H)-CH$_2$CH$_2$B(C$_6$F$_5$)OCH(C$_6$F$_5$)B(C$_6$F$_5$)$_2$(py) **54** (Scheme 8).

The FLP incorporating both secondary phosphine and boranes, MesP(H)C(=CHtBu)B(C$_6$H$_2$(CF$_3$)$_3$)H **55**[39] reacted with CO affording the formaldehyde linkage between B and P in MesPC (=CHtBu)B(C$_6$H$_2$(CF$_3$)$_3$)(μ-OCH$_2$) **56**. Treatment of **56** with N-phenyltriazolindione liberated formaldehyde and led to the formation of the cyclic FLP MesPC(=CHtBu)B(C$_6$H$_2$(CF$_3$)$_3$) (μ-N$_2$(C(O))$_2$NPh) **57** (Scheme 9). In a subsequent 2020 paper, the Erker group[40] described the reaction of the secondary PH/BH derived FLP (tBu$_3$C$_6$H$_2$)P(H)CH$_2$CH$_2$B(C$_6$H$_2$(CF$_3$)$_3$)H **58** with CO, affording the formaldehyde-linked species (tBu$_3$C$_6$H$_2$)P(H) CH$_2$CH$_2$B(C$_6$H$_2$(CF$_3$)$_3$)OCH$_2$B(C$_6$H$_2$(CF$_3$)$_3$)CH$_2$CH$_2$P(H)(tBu$_3$C$_6$H$_2$) **59** in which the CH$_2$O fragment links two boron centres (Scheme 9). In contrast, reaction of **58** with B(C$_6$F$_5$)$_3$ and CO gave (tBu$_3$C$_6$H$_2$)P(H)CH$_2$CH$_2$B(C$_6$H$_2$(CF$_3$)$_3$)CHO$_2$CB(C$_6$F$_5$)$_3$ **60**, while subsequent reaction with pyridine forms a dative bond with B(C$_6$F$_5$)$_3$ and prompted a rearrangement to give the phosphine-oxide in which a CH$_2$ group links the P and B centres, (tBu$_3$C$_6$H$_2$)-P(O)CH$_2$CH$_2$B(C$_6$H$_2$(CF$_3$)$_3$)(CH$_2$) **61**. While this species was a dimer in the solid state, in solution it slowly converted to (tBu$_3$C$_6$H$_2$)P-Me(O)CH$_2$CH$_2$B(C$_6$H$_2$(CF$_3$)$_3$)OP(tBu$_3$C$_6$H$_2$)CH$_2$CH$_2$B (C$_6$H$_2$(CF$_3$)$_3$(CH) **62** (Scheme 9).

3.4 Intramolecular PB$_2$ FLPs

In a 2015 study,[41] the Erker group described the hydroboration of Mes$_2$PCCH with Piers borane followed by the addition of proton and hydride which further underwent a second hydroboration affording Mes$_2$P(H)C(B(μ-H)(C$_6$F$_5$))HCH$_2$B(C$_6$F$_5$)$_2$ **63**. Addition of a second equivalent of Piers borane afforded the FLP containing one phosphorus and two boron centres, Mes$_2$P-(H)C(B(μ-H)(C$_6$F$_5$)$_2$)HCH$_2$B(C$_6$F$_5$)$_2$ **63**. This species reacted with CO at 80 °C, inducing insertion into the B–H bond and C$_6$F$_5$ migration to give Mes$_2$P(H)CHCH(B(C$_6$F$_5$)$_3$) OB(C$_6$F$_5$)(CH$_2$) **64**
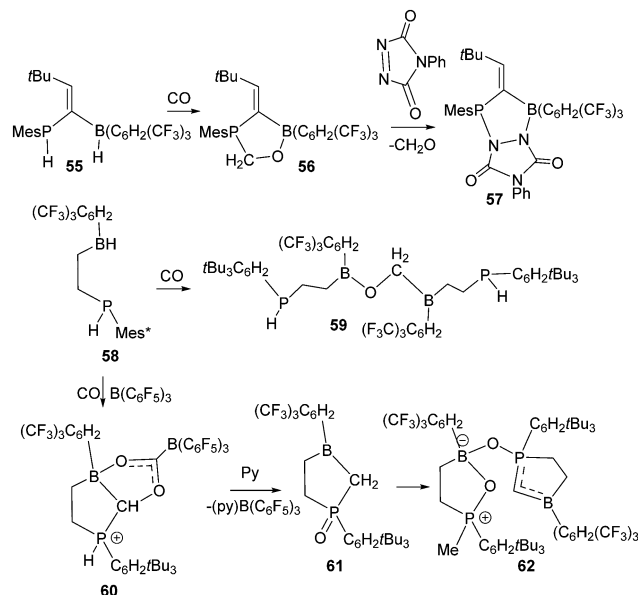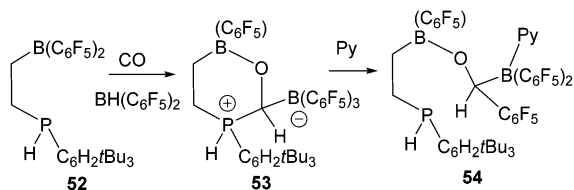
Scheme 9   Reactions of PH-derived FLPs with CO.

(Scheme 10). In a closely related study,[42] hydroboration of the phosphino-ene-yne Ph$_2$PC≡CC(Me)=CH$_2$ and subsequent protonation, treatment with hydride and hydroboration afforded Ph$_2$PCH$_2$CH(Me)(CH(B(C$_6$F$_5$)$_2$))$_2$(μ-H) **65**. This species underwent a similar insertion of CO into the B–H bond, with C$_6$F$_5$ transfer yielding Ph$_2$PCH$_2$CH(Me) (CHB(C$_6$F$_5$)$_2$)CHB-(C$_6$F$_5$)(μ-OCH(C$_6$F$_5$)) **66** (Scheme 10).

A further exploration[43] of related reactions of PB$_2$ FLPs with CO described the reactions of tBu$_3$C$_6$H$_2$P(CH$_2$CH$_2$B(C$_6$F$_5$)$_2$)$_2$ **67** with 9-BBN resulting in the replacement of one C$_6$F$_5$ ring with a hydride giving tBu$_3$C$_6$H$_2$P(CH$_2$CH$_2$B(C$_6$F$_5$)$_2$)(CH$_2$CH$_2$B(C$_6$F$_5$)H) **68**. This species reacted with CO to give tBu$_3$C$_6$H$_2$P(CH$_2$CH$_2$B-(C$_6$F$_5$)$_2$)CH$_2$CH$_2$B(C$_6$F$_5$)(μ-C(H)O) **69**, the product of CO reduction (Scheme 10). Interestingly, the steric demands of the phosphorus substituent altered the chemistry. For example, reaction of C$_6$H$_3$(Mes)$_2$P(CH$_2$CH$_2$B(C$_6$F$_5$)$_2$)$_2$ **70** with CO inducing the insertion of CO into the B–CH$_2$ bond, leading to the ultimate formation of the macrocyclic species [[(Mes)$_2$C$_6$H$_3$PCH$_2$CH$_2$COB(C$_6$F$_5$)$_2$CH$_2$CH$_2$B-(C$_6$F$_5$)$_2$]$_2$ **71** (Fig. 2).[44] Similarly, iPr$_3$C$_6$H$_2$P(CH$_2$CH$_2$B(C$_6$F$_5$)$_2$)$_2$ **72** reacted with CO to give the analogous trimeric species, [iPr$_3$C$_6$H$_2$-PCH$_2$CH$_2$COB(C$_6$F$_5$)$_2$CH$_2$CH$_2$B(C$_6$F$_5$)$_2$]$_3$ **73** (Fig. 2).[44]

3.5 Other main-group FLPs

Van der Vlugt and coworkers[45] reported the synthesis of the salt [Ph$_2$SiCH$_2$(C$_5$H$_3$MeN)][HB(C$_6$F$_5$)$_3$] **74** and its reaction with CO. Computations showed that this proceeds via the generation of a formyl borate anion and an intermediate in which a bora-epoxide is coordinated to the Lewis acidic Si centre. Subsequent C$_6$F$_5$ transfers ultimately effected C–O bond cleavage to give [Ph$_2$SiCH$_2$(C$_5$H$_3$MeN)OB(C$_6$F$_5$)CH(C$_6$F$_5$)$_2$] **75** (Scheme 11). In this case, the Lewis acidic silicon cation and the basic hydrido-borate act to prompt C–O cleavage. It is noteworthy that the corresponding [B(C$_6$F$_5$)$_4$] salt does not react with CO.

Scheme 8   Reaction of secondary phosphine-FLP with CO.

4636 | *Chem. Soc. Rev.*, 2023, **52**, 4632–4643

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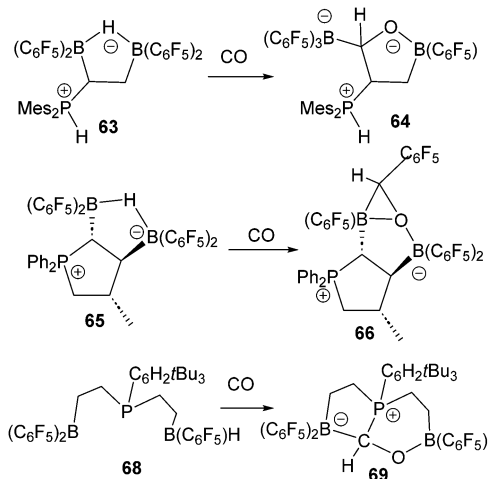
Scheme 10   Reactions of PB₂ FLPs with CO.
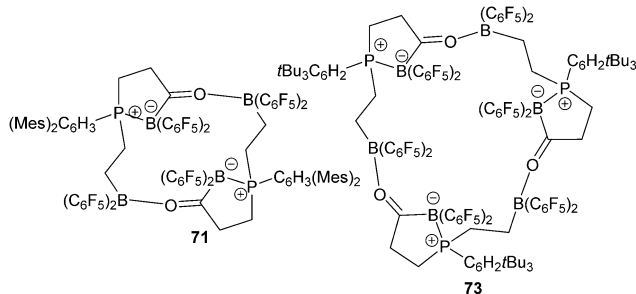
Fig. 2   Macrocyclic products of PB2 FLPs and CO.

3.6   Insights

The work described above extends the variety of B/P FLPs capable of capturing and activating CO. Stoichiometric reactivity affording reduction of CO and in some cases cleavage of the C–O bond. While this is interesting, the use of boon based Lewis acids is seen to led to reactivity of B–C bonds. This finding has inspired the use of other FLP combination targeting the extension of the chemistry towards catalysis.

4. Transition metal FLPs

As FLP chemistry expanded, the notion of what constitutes an FLP has also evolved. Among the earliest expansions of FLP
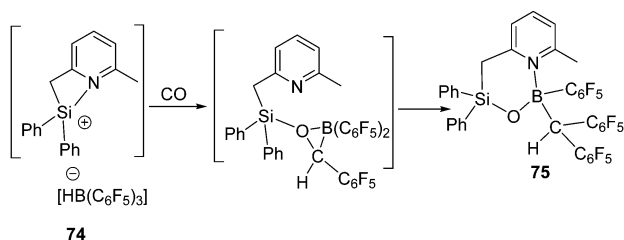
Scheme 11   Reaction of Si-cation complex with CO.
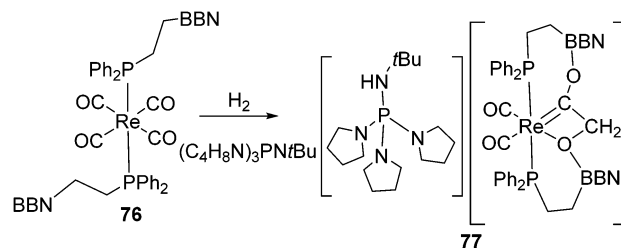
Scheme 12   Re carbonyl FLP complex in reaction with H₂ and base.

chemistry beyond the p-block has been its application in transition metal chemistry.[46,47]

In a very early use of FLP type ligands in transition metal chemistry, Bercaw and coworkers[48] described the reaction of the Re carbonyl species $(Ph_2PCH_2CH_2(9\text{-}BBN))_2Re(CO)_4$ **76** with H₂ in the presence of the strong base $(C_4H_8N)_3PNtBu$. This resulted in the reduction of CO affording the salt $[(C_4H_8N)_3PNtBuH]$ $[(Ph_2PCH_2CH_2(9\text{-}BBN))_2Re(CO)_2(COCH_2O)]$ **77** (Scheme 12). In this case, further experimental data showed that the activation of H₂ was affected by the FLP derived from the base and the pendant borane in the Re complex.

In another 2011 study, Wass and corworkers[49] explored the incorporation of early-metal centres as the Lewis acid centre of FLPs. While the Zr cation with a pendant phosphine in $[Cp*_2Zr(ClPh)OC_6H_4P(tBu)_2][B(C_6F_5)_4]$ **78** captured CO to give $[Cp*_2Zr(CO)OC_6H_4P(tBu)_2][B(C_6F_5)_4]$ **79**, no interaction with the pendant basic phosphine was observed. This was attributed to the exceptionally high Lewis acidity of the Zr cation. In a similar sense, some years later, Erker and coworkers[50] reported the related reaction of $[Cp_2ZrC_6H_4PPh_2][B(C_6F_5)_4]$ **80** with CO which led to insertion of CO into the Zr–C bond affording the Zr-acyl cation $[Cp_2ZrC(O)C_6H_4PPh_2][B(C_6F_5)_4]$ **81**. Again, the phosphine fragments only served to stabilize the Zr cation and does not participate in the reaction with CO.

Nonetheless, Wass and his team continued to explore transition metal derived FLPs. In one study[51] they described the FLP derived from the electron rich Pt(0) species $C_6H_4(CH_2PtBu_2)_2Pt(CH_2CH_2)$ **82**
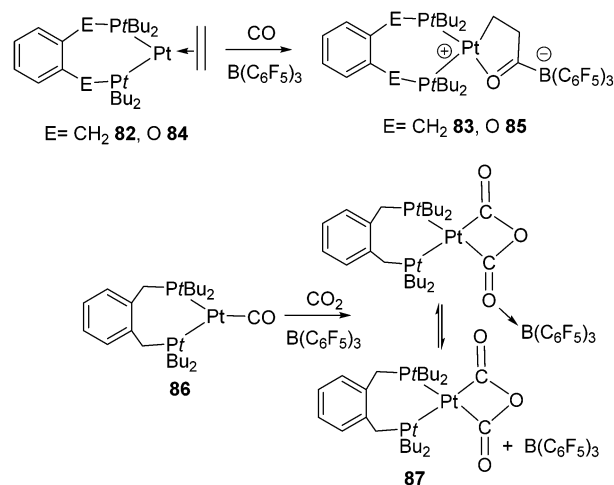
Scheme 13   Reactions of Pt(0)/B based FLPs.

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Chem. Soc. Rev., 2023, **52**, 4632–4643 | **4637**

with B(C$_6$F$_5$)$_3$. The reaction with CO resulted in the zwitterion C$_6$H$_4$(CH$_2$PtBu$_2$)$_2$PtCH$_2$CH$_2$C(O)B(C$_6$F$_5$)$_3$ **83** (Scheme 13). In this case, CO adds to the olefin affording a five-membered metallocycle. Related chemistry was seen for the analogue C$_6$H$_4$(OPtBu$_2$)$_2$-Pt(CH$_2$CH$_2$) **84**,[52] affording the product C$_6$H$_4$(OPtBu$_2$)$_2$PtCH$_2$CH$_2$-C(O)B(C$_6$F$_5$)$_3$ **85** (Scheme 13). Interestingly, the species C$_6$H$_4$-(CH$_2$PtBu$_2$)$_2$Pt(CO) **86** was shown to react with CO$_2$ in the presence of B(C$_6$F$_5$)$_3$ to give the product of CO$_2$ addition C$_6$H$_4$(CH$_2$PtBu$_2$)$_2$-Pt(C(O))$_2$O **87** (Scheme 13) that reversibly binds to the borane.[51]

4.1 Insights

While the work with transition metal FLPs and CO is limited, it does indicate that the concept can be applied to such systems, affording both CO capture and unique subsequent reactivity. This is an area, in which FLP are used in a cooperative fashion with transition metal chemistry is one that certainly has considerable potential for further development.

5. Alkali-metal species as FLPs

The FLPs discussed above exploit combinations of electron-rich nucleophiles and electrophiles. In such cases, steric demands weaken dative bonding allowing the generation of the FLP. In the case of alkali-metal species, an analogous combination of a nucleophilic anion and a Lewis acidic metal ion present only electrostatic attractions thus precluding quenching of the acidity and basicity, directly analogous to FLPs. Indeed this perspective is consistent with our report in 2018, where we showed that group 1 metal-amides and -phosphides could be used to reversibly activate H$_2$ and to effect hydrogenation catalysis.[53] This ability of alkali-metal species to behave as an FLP with H$_2$ prompted the examination of the reactivity of such species with other small molecules including CO. Certainly in the older literature, nucleophilic attack of CO by organolithium,[54–64] Grignard[65,66] and amides reagents[67–70] has been extensively studied. However, our efforts have brought a new perspective to this chemistry as typically in the older work, the role of the Lewis acidic alkali metal is rarely considered.

5.1 Alkali-metal phosphides and CO

In considering the reactions of alkali-metal phosphides with CO, we note the use of NaPH$_2$ to prepare sodium phosphaethynolate (NaOCP) in 2011. While this reaction occurs under forcing conditions, it demonstrates nucleophilic attack at carbon of CO by phosphide.[71] More recently, we reported the related reaction of KPtBu$_2$ with CO under mild conditions. In this case, the formation of a transient anionic acyclic carbene is thought to induce a 1,2-$tert$-butyl group migration affording the acyl-phosphide anions [(18-crown-6)K·THF$_2$][E-tBuP=C(tBu)O] **88** as the major product (Scheme 14). Dimerization of the transient carbene gave lesser amounts of [K$_6$(18-crown-6)][(tBu$_2$PCO)$_2$]$_3$ **89** containing the ene-diolate dianions (Scheme 14). The formation of the former species **88** is favoured under UV irradiation.

In a similar fashion, **88** also reacted as a nucleophile with CO although the reaction was slow at ambient temperature. After 28 days, the species [K(18-crown-6)][(OCtBu)$_2$P] **90** was
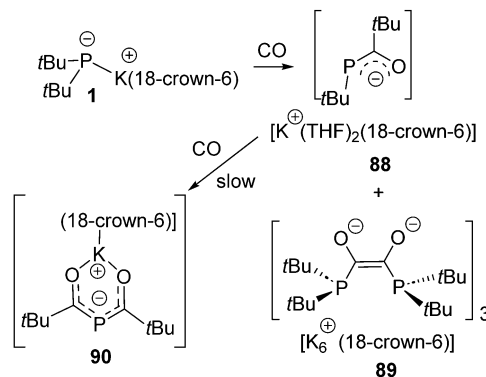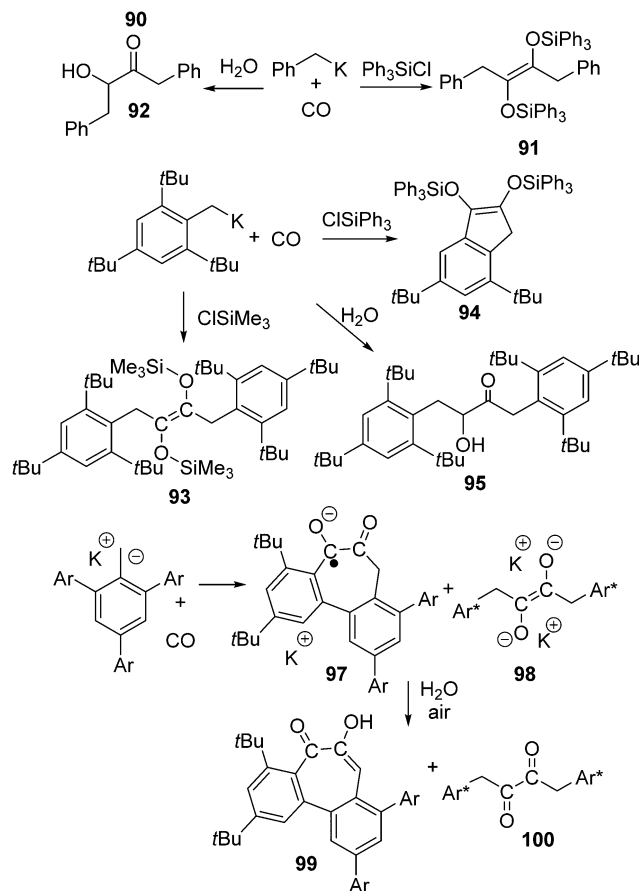

Scheme 14 Reactions of alkali-metal phosphides with CO.

formed and isolated (Scheme 14 similar to the formation of **88**, nucleophilic attack of the P of **88** at CO with subsequent 1,2-$tert$-butyl migration to carbon. Related diacyl-phosphides were reported by Becker[72–74] and Grützmacher[75,76] while Goicocechea described related bis-carbamoyl phosphides.[77] In related syntheses, phosphide attack of the CO fragment of Ph$_3$GePCO[78] was used to generate a series of diphospha-ureas of the form (tBu)$_2$PC(O)PR$_2$ (R = GePh$_3$, Me).[79]

5.2 Alkali-metal carbanions and CO

Analogous reactions of benzyl potassium derivatives with CO generate carbene-like intermediates as evidenced by the treatment of PhCH$_2$K with CO and quenching with Ph$_3$SiCl afforded the tetra-substituted olefin (PhCH$_2$C(OSiPh$_3$))$_2$ **91**.[80] On the other hand, hydrolysis of the reaction mixture afforded PhCH$_2$C(O)CH(OH)CH$_2$Ph **92** (Scheme 15). The more sterically hindered benzyl potassium, K[2,4,6-(tBu)$_3$C$_6$H$_2$CH$_2$] reacted with CO and subsequent addition of Me$_3$SiCl gave the related olefinic species ((Me$_3$SiO)(2,4,6-(tBu)$_3$C$_6$H$_2$CH$_2$)C)$_2$ **93** as the major product (Scheme 15). In contrast, quenching the reaction with Ph$_3$SiCl afforded the fused ring product tBu$_2$C$_6$H$_2$(C(O-SiPh$_3$)C(OSiPh$_3$)CH$_2$) **94**. Quenching the reaction with water anaerobically, afforded α-hydroxy ketone (2,4,6-(tBu)$_3$C$_6$H$_2$)CH$_2$-C(O)CH(OH)CH$_2$(2,4,6-(tBu)$_3$C$_6$H$_2$) **95** (Scheme 15) while the 1,2-diketone species (2,4,6-(tBu)$_3$C$_6$H$_2$CH$_2$CO)$_2$ **96** was favoured if the hydrolysis was performed in air. An even bulkier benzyl potassium derivative K[2,4,6-(3,5-tBu$_2$C$_6$H$_3$)$_3$C$_6$H$_2$CH$_2$] reacted with CO to yielded a paramagnetic product **97**, formulated as the radical anion salt K[3,5-(tBu)$_2$C$_6$H$_2$C(O)C(O)CH$_2$C$_6$H$_2$-(C$_6$H$_3$3,5-(tBu)$_2$)$_2$]$^•$ on the basis of EPR data, while NMR data revealed the concurrent formation of the diamagnetic bis-alkoxide salt **98** (Scheme 15). Quenching the reaction with water provided the seven-membered aromatic species [3,5-(tBu)$_2$C$_6$H$_2$C(O)C(OH)CHC$_6$H$_2$(C$_6$H$_3$3,5-(tBu)$_2$)$_2$] **99** and the diketone ((2,4,6-(3,5-tBu$_2$C$_6$H$_3$)$_3$C$_6$H$_2$CH$_2$C(O))$_2$ **100**. A further study examined the reaction of the dilithio-species [(Ph$_2$P(S))$_2$-CLi$_2$(THF)]$_2$[81] in reaction with CO at room temperature. This led to the formation of a new C–C bond and migration of one of the phosphine-sulphide fragment affording the species formulated as [Ph$_2$P(S)CC(P(S)Ph$_2$)O]Li$_2$ **101**. Although this species was not isolated, treatment with wet Et$_2$O led to the isolation of
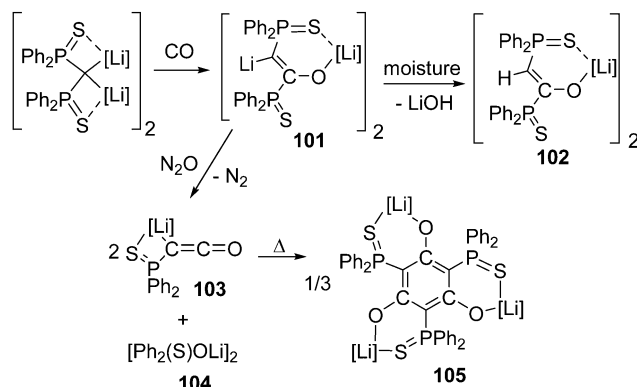
4638 | *Chem. Soc. Rev.*, 2023, **52**, 4632–4643

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Scheme 15 reactions of benzyl-potassium species with CO.

Scheme 16 Reactions of dilithio-species with CO.

[Ph₂P(S)CHC(P(S)Ph₂)OLi(THF)]₂ **102** (Scheme 16). Exposure of solutions of **101** to 1 atm N₂O at room temperature generated the anionic ketene Ph₂P(S)CCOLi(THF)₂ **102** and the by-product [Ph₂P(S)OLi(THF)₂]₂ **104** (Scheme 16). Heating of the mixture of **103**/**104** resulted in the cyclotrimerization of **103**, generating the hexa-substituted benzene species [Ph₂P(S)CCOLi(THF)₂]₃ **105** (Scheme 16) in an overall yield of 72%. It is noteworthy that a subsequent paper by Gessner and coworkers[82] isolated and structurally characterized **103** derived from the reaction of [Ph₂P(S)CHKPPh₃] with CO. This strategy effects displacement of the PPh₃, generating the metalated ketene K[Ph₂P(S)CCO]. Subsequent reaction with a range of electrophiles affords a series of ketenes and related compounds.

5.3 Alkali-metal amides and CO

As early as 1965, Na[N(SiMe₃)₂] was reported to react with CO at 80 °C and 100 atm pressure in hydrocarbon or aromatic solvent to generate NaCN.[83] Recently we reported the analogous reaction of K[N(SiMe₃)₂] in C₆D₆ with 1 atm pressure of CO for 24 h at room temperature followed by heating to 50 °C for a further 24 h. This led to the formation of KCN in 64% yield. Repeating the reaction in THF at 50 °C improved the yield to 89% and the yield was further improved to 99% with the addition of 18-crown-6 and the use of 1,4-dioxane as the solvent. While under these latter conditions [[18-crown-6)KCN] **106** was isolated (Scheme 17), this

protocol also provides an easily modifiable, transition metal-free route to ¹³CN⁻. Mechanistically, this reaction is thought to proceed *via* nucleophilic attack of CO by amide, generating a carbene-like species. This species undergoes an 1,3-silyl group migration and elimination of siloxide to generate cyanide. This view was largely supported by DFT computations, although the intermediary isocyanide, Me₃SiNC, was revealed. This prompted the corresponding reactions of sterically demanding silylamides of the form [(Me₃Si)(R)N]M **107** (M = Li or K, R = tBu, adamantyl, 2-iPrC₆H₄, 2-PhC₆H₄, 2-Me-4-MeOC₆H₃, 2,6-Me₂C₆H₃, 2,6-iPr₂C₆H₃, 2,4,6-(tBu)₃C₆H₂, 2,6-(Ph₂CH)₂-4-MeC₆H₂) with CO. In all cases, the corresponding isocyanides, **108** were obtained in yields ranging from 71 to 97% (Scheme 17).

For sterically less demanding amides, Seyferth had reported some years ago that the reaction with CO afforded silylation of amidocarbomoyl lithium species derived from 1,2 silyl-migration.[84,85] This prompted us to employ a more sterically demanding silyl-group to encourage 1,3-silyl migration. Indeed, for amides of the form [(Ph₃Si)(R)N]M **109** (M = Li or K, R = 4-MeOC₆H₄, iPr, Bu, hexyl C₆H₅, 3-MeOC₆H₄, 4-Me₂NC₆H₄, 4-PhOC₆H₄, 4-iPrC₆H₄, 2-picolyl) with CO, the corresponding
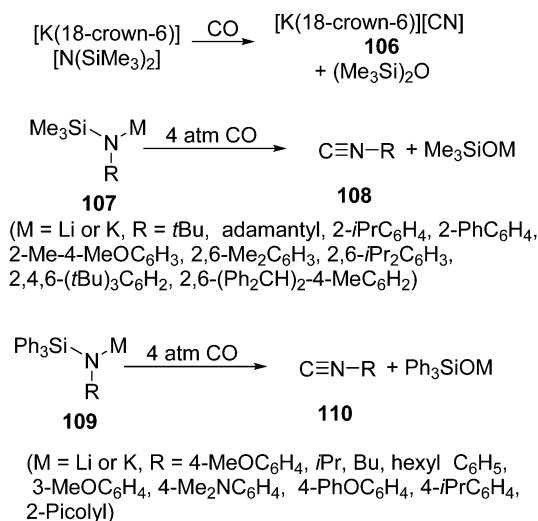
Scheme 17 Reactions of silyl-amides with CO.

isocyanides **110** were obtained in yields of 74–95% (Scheme 17). This facile protocol to isocyanides from CO and amide proved scalable to the gram scale and also provided a convenient route to the incorporation of a ^{13}C label.

In another study, we targeted reactions of amides with substituents that would not migrate. To this end, Cy$_2$NLi (Cy = cyclohexyl) was reacted with 1 atm of CO. After 12 h, and following hydrolysis, high resolution mass spectrometry (HRMS) revealed a series of species of the formulae (Cy$_2$N)$_2$(CO)$_n$H$_2$ (n = 2–4) and (Cy$_2$N)$_3$(CO)$_n$H$_3$ (n = 3–7) consistent with homologation of CO. Slow evaporation of a THF extract of the reaction residue afforded Cy$_2$NC(O)CH(OH)NCy$_2$ **111** which was isolated and fully characterized (Scheme 18). Alternatively, quenching the above reaction with Cy$_2$BCl afforded the isolation of (Cy$_2$B)(OCNCy$_2$)$_2$COBCy$_2$ **112** and (Cy$_2$NCOBCy$_2$)$_2$C(μ-O) **113**, respectively (Scheme 18). While the former species was the major product, these species are isomers which incorporate three molecules of CO. The analogous reaction of Cy$_2$NLi was using 4 atm of CO for 12 h at room temperature and quenching with Cy$_2$BCl provided (Cy$_2$NC(O)-CO)$_2$(BCy$_2$)$_2$ **114** derived from the catenation of four CO molecules (Scheme 18).

In the context of the homologation of CO by alkali metal species salts, it is noteworthy that a series of intriguing papers from the groups of Jones[18,86–89] and Hill[90,91] have emerged in which reduced alkaline earth metal-species have been shown to effect CO homologation affording a variety of interesting species. Although this chemistry is not FLP chemistry, it does reflect the combined action of an electron source and a Lewis acidic centre, effecting the activation of CO.

Given the above demonstration of CO homologation, this prompted an investigation of reactions with concurrent exposure to H$_2$. Thus, reaction Cy$_2$NLi with a 1 : 1 mixture of H$_2$/CO was performed and the hexameric species [Cy$_2$NCH$_2$OLi]$_6$ **114** was found amongst the residues. In addition, the mass spectrometry showed the formation as Cy$_2$NC(O)CH$_2$OH, **115**. These products infer the generation of a carbene-type intermediate which reacts with H$_2$ to give **114** or with CO and subsequently H$_2$ to give **115** (Scheme 19). This notion was supported *via* isotopic labelling experiments which afforded the various isotopomers of **115**.
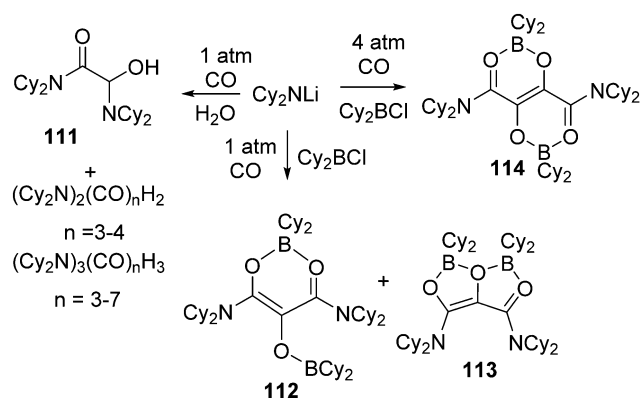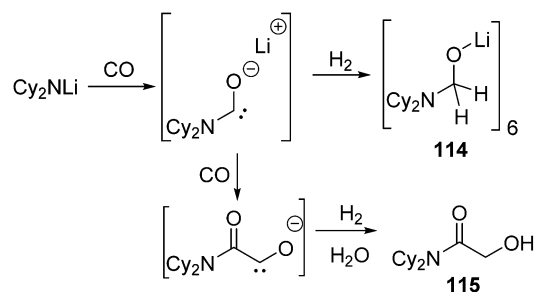
A detailed computational study of these reactions showed the sequence of steps involving CO homologation were energetically accessible. At the same time, reaction of each of the intermediates with H$_2$ was also accessible with slightly higher activation barriers, creating a competitive reaction pathway. While both C–C and C–H bond formations are accessible, the course of the reaction will be altered by the partial pressures of CO and H$_2$. To our knowledge, this represents the first main group system to effect sequential C–C and C–H bond formations from CO and H$_2$, the fundamental reactions of the transition metal mediated Fischer–Tropsch process.[92]

5.4 Insights

The chemistry above demonstrates that viewing alkali metal species as FLPs is a credible approach. Simple amide and phosphide salts are shown to react with CO affording routes to C–C coupling products. Use of silyl amides provides routes to cyanide and isocyanides, while dialkyl amides afford unprecedented avenues to CO homologation and further reactions with H$_2$. These fundamental steps of Fischer–Tropsch chemistry under such remarkably mild conditions, suggest that further optimization of both the FLP and reactions conditions could provide reduction products of higher homologues of CO such as poly-ols, sugars or hydrocarbons.

6. Heterogeneous FLPs

A variety of heterogeneous systems have been described which incorporate or behave as FLPs. These include surface-modified Au, polymers incorporating phosphine and borane units, molecular sieves, 2D materials and metal oxides. As the studies of such materials is relatively new, most applications have involved hydrogenation. This material has been recently reviewed.[93] While several such system have been explored for hydrogenation and CO$_2$ reduction catalysis,[94–100] reactions of CO with heterogeneous FLPs have drawn less attention to date. In 2019, Chen *et al.*[101] described computations that considered the incorporation of boron decorated on a C$_2$N monolayer. The results suggested this material is an efficient photocatalyst for CO reduction to C$_2$H$_4$ and C$_3$H$_6$. Most recently, Guo *et al.*[102] described the preparation of Au decorated hydroxyapatite (HAP)-CeO$_2$. Employing a variety of spectroscopies, the Lewis acidic Ce^{3+} and a Lewis basic OH$^-$ group on the surface were shown to enable the activation of O$_2$ facilitating CO oxidation.

Scheme 18 Reactions of Cy$_2$NLi with CO.

Scheme 19 Reactions of Cy$_2$NLi with syngas.

4640 | *Chem. Soc. Rev.*, 2023, **52**, 4632–4643

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6.1 Insights

The description of the reactivity sites on surfaces as FLPs provides a new perspective on the design of heterogeneous catalysts. In addition, as these heterogeneous catalysts are effective in mediating the reduction or deoxygenation of CO, this further inspires molecular chemists to develop new FLP systems that mimic the reactivity of the heterogeneous systems.

7. Future perspective

The range of small molecules that are captured and activated by FLPs has grown since the concept was first articulated in 2006 and 2007. This review has summarized progress in the FLP chemistry of CO. This work demonstrates the ability of classic B/P as well as a range of main group and transition metal FLPs to capture CO.

While the establishment of the ability of FLPs to capture CO is interesting, the more recent work from Aldridge's group clearly illustrates the potential for the advancement in CO sensing technologies. On the other hand, various p-block FLP systems are shown to undergo reactivity with CO and reducing agents, although such FLPs can also participate themselves in the reactivity, thus precluding an avenue to catalysis. Nonetheless, these studies lay the fundamental groundwork for the development of synthetic applications. Extension of the concept to transition- and s-block metal species illustrates not only the wider implications of the FLP concepts, but also unveiled strategies to CO homologation. In addition, in the presence of syn-gas, these systems demonstrate the fundamental steps in Fischer–Tropsch chemistry. These observations infer that C–C and C–H activations are both energetically accessible under mild conditions and suggest that tuning of the nature of the alkali metal FLP or perhaps other FLP systems could offer a strategy to favour higher CO homologs, suggesting the potential of transition metal-free routes to poly-ols, sugars or hydrocarbons.

It is clear from the findings described herein, that while the concept of FLPs has evolved dramatically over the last almost two decades, it is now at a stage where it can provide a fundamentally unique approach to the challenging issues in small molecule chemistry and catalysis. While this review has focused on recent advances in FLP-CO chemistry, it is intriguing to consider that CO and N_2 are isoelectronic. This notion suggests that chemists may begin to apply the lessons learned from FLP-CO chemistry to the challenge of metal-free Haber–Bosch chemistry. While is tough to predict what the future holds, it is clear that chemists will continue to develop new and exciting metal free chemistry by exploiting the notion of cooperative action of electron donors and acceptors.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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4642 | *Chem. Soc. Rev.*, 2023, **52**, 4632–4643

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Chem. Soc. Rev., 2023, **52**, 4632–4643 | **4643**