This indicates that the LUMO is nondegenerate for this isomer.

The electrochemical data for the  $D_2$  and  $D_{2d}$  isomers are in full agreement with those previously reported<sup>[13]</sup> except for a recent publication by Anderson et al.<sup>[14]</sup> The latter group investigated the electrochemistry of two isomers (Table 3) that were separated by HPLC and, on the basis of the relative abundances and previous work, were assigned the  $D_2$ - and  $D_{2d}$ -symmetrical structures. While the redox properties of the  $D_2$  isomer match those reported here, the ones assigned to the  $D_{2d}$  isomer differ from those determined by us and others<sup>[13]</sup> for this fullerene and rather match those of what we call here the "new isomer". On the basis of our findings we conclude that Anderson et al. had not isolated  $D_{2d}$ - $C_{84}$  but rather the "new isomer" in addition to the  $D_2$ -symmetrical one.

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### A Polymer-Supported Phosphazine as a Stable and Practical Reagent in the Three-Component Synthesis of Substituted (Cyclopentadienyl)tricarbonylrhenium Complexes\*\*

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In recent years the use of reagents and catalysts bound to inorganic and organic solid supports has rapidly become an area of intense research activity,<sup>[1]</sup> since they present several obvious advantages over their soluble counterparts: they can be removed from the reaction mixture by simple filtration and, often, can be recycled and used again. Herein we report the preparation and the use of a polymer-bound stabilized diazocyclopentadiene ( $C_5H_4N_2$ ) analogue, which can be used as a safe and storable source of  $C_5H_4N_2$  in the synthesis of substituted cyclopentadienyl–Re(CO)<sub>3</sub> complexes.

The use of "free"  $C_5H_4N_2$  in the synthesis of halogensubstituted cyclopentadienyl complexes of rhenium was

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reported more than twenty years ago.<sup>[2]</sup> Recently, however, we found that C5H4N2 reacts simultaneously with a [fac-Re- $(CO)_3$ <sup>+</sup> precursor<sup>[4]</sup> and external nucleophiles, such as carboxylates<sup>[3a]</sup> efficiently, to produce acyloxy-substituted cyclopentadienyl-Re(CO)<sub>3</sub> complexes in a one-pot reaction (threecomponent reaction) and in short times. We then extended the scope of this reaction to the synthesis of carbon-substituted cyclopentadienyl-Re(CO)<sub>3</sub> complexes by utilizing boronic acids as carbon nucleophiles;<sup>[3b]</sup> this transformation represents a new method for C-C bond formation that is based on boronic acids, but does not require a catalyst such as palladium. These results were very encouraging, especially in view of a possible use of this reaction for radiolabeling biologically interesting molecules with cyclopentadienyltricarbonyl complexes containing <sup>186</sup>Re, <sup>188</sup>Re, and <sup>99m</sup>Tc radionuclides. However, a major limitation for an application of the three-component synthesis to the routine preparation of radiopharmaceuticals was the high instability of C5H4N2.[5] In fact, this key reagent must always be stored in solution,<sup>[6]</sup> usually in pentane, at low temperatures (for example,  $-40^{\circ}$ C), in the dark; yet, in spite of all these precautions, it cannot be stored for longer than a few weeks, because of its rapid decomposition. All these aspects constituted a serious limitation to the practical utilization of this reaction in medical facilities. Therefore, we started to look for alternative reagents that possesed the same good reactivity of C<sub>5</sub>H<sub>4</sub>N<sub>2</sub>, together with better stability and handling properties. We focused our attention on an adduct of C5H4N2 with triphenylphosphane, phosphazine 1,<sup>[7]</sup> which was known to be a stable compound under ambient conditions (moist air, room temperature, light, shocks).<sup>[8]</sup> As a matter of fact, 1 is used in the gravimetric titration of solutions of diazocyclopentadiene.<sup>[8b]</sup> We were pleased to find that **1** readily dissociates into Ph<sub>3</sub>P and free diazo compound when dissolved in acetonitrile, which is the solvent used in our reaction [Eq. (1)].<sup>[3]</sup> At 23 °C



the dissociation of **1** is considerable [Eq. (2), the  $K_{\text{diss}}$  value is obtained by NMR analysis of a solution of **1** in [D<sub>3</sub>]acetoni-trile at equilibrium], and under typical reaction conditions

$$K_{\rm diss} (23 \,^{\circ}{\rm C}) = \frac{[{\rm C}_{5}{\rm H}_{4}{\rm N}_{2}][{\rm Ph}_{3}{\rm P}]}{[1]} = 4.0 \times 10^{-3} \,\,{\rm mol}\,{\rm L}^{-1} \tag{2}$$

(80 °C), further dissociation generates levels of free  $C_5H_4N_2$  that are sufficient for an efficient reactivity, as we could verify in preliminary experiments with carboxylates. However, the presence of free triphenylphosphane in the reaction mixture, produced by the dissociation of **1**, made the purification of the products very awkward, because it was difficult to separate the phosphane from most of the product complexes. This resulted in a decrease in the product yields when **1** was used in place of free  $C_5H_4N_2$ .

To overcome this problem, we envisaged the use of a polymer-bound phosphazine **2**, so that the phosphane formed at the end of the reaction could be removed by filtration, thereby considerably simplifying the work-up and purification procedure. The heterogeneous reagent **2** was prepared by treating a dichloromethane suspension of triphenylphosphane bound to a polystyrene support  $3^{[9]}$  with a pentane solution of  $C_5H_4N_2$  [Eq. (3)]. The functionalization of the polymer was very efficient (85%) after only 2 hours at room temperature.



The amount of  $C_5H_4N_2$  in the heterogeneous reagent 2 was determined by several methods. Determination of the amount of nitrogen (%N) by elemental analysis can be used as a measurement of the extent of functionalization, but elemental analysis by itself does not distinguish between the C<sub>5</sub>H<sub>4</sub>N<sub>2</sub> that is covalently bound and thereby stabilized as a phosphazine and material that may simply be trapped in the polymeric network, but still remaining as a free unstable diazo compound. In order to be sure that all unreacted C5H4N2 had been washed out of the polymer, we analyzed 2 by IR and solidstate NMR spectroscopy. Free C5H4N2 has a very strong, characteristic IR absorption around 2100 cm<sup>-1</sup> which arises from the asymmetric stretching of the cumulated C-N-N double bonds. The absence of such a band in the product polymer 2 (as was also the case in the monomeric phosphazine 1), indicated that the amount of nitrogen found by elemental analysis could be entirely attributed to polymer-bound phosphazine. In fact, other typical bands for phosphazines were found in the IR spectrum of 2 at  $\tilde{\nu} = 1517 (v_{C=N}), 1102$ ( $\nu_{P=N}),$  and 974 cm  $^{-1}$  ( $\nu_{N-N}).$ 

To further validate these results, we conducted a solid-state "magic angle spinning" (MAS) <sup>31</sup>P NMR analysis of **2** (Figure 1). The <sup>31</sup>P spectrum shows two peaks, an intense one at  $\delta = 21.10$ , which corresponds to functionalized P atoms, and a weaker one at  $\delta = -7.03$ , which arises from unreacted phosphane groups present in the polymer. The observed chemical shifts compare favorably to those found in the <sup>31</sup>P NMR spectra of their soluble counterparts in CDCl<sub>3</sub>: free phosphazine **1** gives a reasonance at  $\delta = 23.23$ , and Ph<sub>3</sub>P at  $\delta = -2.29$ . The <sup>31</sup>P MAS NMR spectrum of the starting polymeric phosphane **3** also showed a single peak at  $\delta =$ -6.77, which confirmed the identity of the weaker peak shown in Figure 1.

As we expected, the striking feature of 2 was its great stability. This material shows no sign of decomposition (elemental analysis, NMR and IR spectroscopy) after many months (up to 11 as of yet) of storage on the bench, exposed to ambient conditions without any particular precautions. To test its reactivity, 2 was then used in the three-component reaction with several nucleophiles. The yields obtained using heteroatom nucleophiles (Br<sup>-</sup> and carboxylates) according to

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Figure 1. <sup>31</sup>P MAS NMR (121 MHz) spectrum of 2.

Equation (4) (L = CH<sub>3</sub>CN) are summarized in Table 1. Interestingly, **2** showed the same good reactivity as free  $C_3H_4N_2$ .<sup>[3a]</sup>



Table 1. Comparison of the yields of the isolated substituted cyclopentadienyl–Re(CO)<sub>3</sub> complexes **6** obtained with heteroatom nucleophiles **5** from free diazocyclopentadiene or the polymer-supported reagent **2** [Eq. (4)].

Entry	Nu <sup>-</sup>		Product	$\begin{array}{l} Yield [\%]^{[a]} \text{ with} \\ C_5 H_4 N_2^{[b]}  2^{[c]} \end{array}$	
1	Br- 5a		6a	67	71
2	Сн₃́(О-	5b	6b	69	67
3	сн <sub>3</sub> -о-	5c	6c	59	60
4	но-	5d	6d	72	71
5	PhO Boc-NH O-	5e	6e	60	64

[a] Yields of complexes purified by column chromatography are based on the initial rhenium precursor  $(Et_4N)_2[ReBr_3(CO)_3]^{[10]}$  used to prepare compound **4** in situ.<sup>[3a]</sup> [b] See ref. [3 a]. [c] 0.050 mmol of **4**, 0.10 mmol of nucleophile, 39 mg of **2** (containing 0.075 mmol of C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>), 2.5 mL of CH<sub>3</sub>CN, 80 °C, 45 min; carboxylates **5b**, **5d**, and **5e** were generated in situ by treating the correspondent carboxylic acid (0.1 mmol) with 0.2 mmol of Et<sub>3</sub>N; commercially available sodium salt of **5c** was used.

The results obtained in the more recently described reaction involving boronic acids as carbon nucleophiles [Eq. (5)] are reported in Table 2. Here, the yields obtained with **2** are generally slightly lower (apart from entry 2) than



Table 2. Comparison of the yields of the isolated substituted cyclopentadienyl-Re(CO)<sub>3</sub> complexes 8 obtained with boronic acids 7 using free diazocyclopentadiene or the polymer-supported reagent 2 [Eq. (5)].

Entry	Boronic acid	R	Complex	$\begin{array}{c} \mbox{Yield}  [\%]^{[a]}  \mbox{with} \\ \mbox{C}_5 \mbox{H}_4 \mbox{N}_2^{[b]} \mbox{$2^{[c]}$} \end{array}$	
1	7a		8a	64	53
2	7 b	CH3	8b	34	41
3	7 c	СН3О-	8c	74	56
4	7 d	n-C7H15	8 d	51	45
5	7e	s	8e	72	50

[a] See Table 1. [b] See ref. [3b]. [c] 0.050 mmol of 4, 0.50 mmol of boronic acid, 1.0 mmol of Et<sub>3</sub>N, 39 mg of 2 (containing 0.075 mmol of  $C_5H_4N_2$ ), 2.5 mL of CH<sub>3</sub>CN, 80 °C, 45 min.

the ones obtained with  $C_5H_4N_2$ ,<sup>[3b]</sup> but are still in a respectable range (around 50%), considering that this complex transformation results in the simultaneous formation of a carbon – carbon  $\sigma$  bond and an  $\eta^5$ -cyclopentadienyl – rhenium bond. It is important to emphasize the great tolerance of this reaction towards a wide variety of functional groups, including alcohols, phenols, amides, and ketones. Moreover, this reaction is tolerant to sulfur-containing heterocycles such as thiophenes as shown by the synthesis of a novel thienyl-substituted complex **8e** (Table 2, entry 5).

In conclusion, the solid-phase reagent **2** described herein combines great safety, handling, and excellent storage properties, with good reactivity in the synthesis of substituted cyclopentadienyl– $\text{Re}(\text{CO})_3$  complexes. Its consequent suitability for kit-formulations should facilitate the use of the three-component reaction for the preparation and use of these radiopharmaceuticals that contain organometallic complexes of  $\text{Re}^I$  and, by chemical analogy,  $\text{Tc}^{I[11]}$  in medical facilities, applications that would not be possible if it were necessary to use highly unstable reagents such as free diazocyclopentadiene. Furthermore, the availability of this supported/stabilized cyclopentadienyl-ring precursor should make the synthesis of half-sandwich complexes containing other metals practical.

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#### **Experimental Section**

Diazocyclopentadiene (1.78 m in pentane) was prepared by a literature method.<sup>[6b]</sup> Polymer-supported triphenylphosphane **3** and all other chemicals were obtained from commercial sources unless otherwise specified. Boronic acid (**7d**) was prepared from 1-nonyne by a literature method.<sup>[12]</sup> Characterization data and purification details of complexes 6a,<sup>[2]</sup> 6b - e,<sup>[3a]</sup> and 8a - d<sup>[3b]</sup> have already been reported.

**2**: A 1.78 m pentane solution of diazocyclopentadiene (4 mL, 1.2 equiv) was added to a well stirred suspension of the heterogeneous phosphane **3** (2.0 g,  $\approx$  5.6 mmol of P) in CH<sub>2</sub>Cl<sub>2</sub> (15 mL) at room temperature. The mixture was stirred for a further 2 h, after which time Et<sub>2</sub>O (30 mL) was added and the orange insoluble polymer was collected by filtration, washed with Et<sub>2</sub>O (3 × 10 mL), and dried under vacuum to yield **2** (2.4 g) as an orange powder. Elemental analysis revealed 5.39 %N, which corresponded to a 85 % functionalization of the phosphane groups. IR (CH<sub>2</sub>Cl<sub>2</sub> film):  $\tilde{\nu}$  = 1517 (C=N), 1102 (P=N), 974 cm<sup>-1</sup> (N–N); <sup>31</sup>P MAS NMR (121 MHz, neat solid, external reference: H<sub>3</sub>PO<sub>4</sub>, see Figure 1):  $\delta$  = 21.10 (phosphazine), -7.03 (phosphane).

**8e** (Table 2, entry 5): m.p. 86 °C;  $R_{\rm f}$  (silica gel, hexane) 0.14; IR (KBr):  $\bar{\nu}$ = 2018 (CO<sub>asym</sub>), 1910 cm<sup>-1</sup> (CO<sub>sym</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.32 (dd, J = 5.0, 2.9 Hz, 1H, H5 thienyl), 7.28 (dd, J = 2.9, 1.5 Hz, 1H, H2 thienyl), 7.07 (dd, J = 5.0, 1.5 Hz, 1H, H4 thienyl), 5.67 (pseudo t, J = 2.2 Hz, 2H, Hα C<sub>5</sub>H<sub>4</sub>Ar), 5.37 (pseudo t, J = 2.2 Hz, 2H, Hβ C<sub>5</sub>H<sub>4</sub>Ar); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  = 194.04 (CO), 132.72 (C4 thienyl), 126.64, 126.20, 121.59 (C3 thienyl), 103.91 (C4 C<sub>5</sub>H<sub>4</sub>Ar), 84.01, 81.63 (C3 C<sub>5</sub>H<sub>4</sub>Ar); MS (70 eV): m/z (%): 418 (100) [ $M^+$ , <sup>187</sup>Re], 416 (62) [ $M^+$ , <sup>185</sup>Re], 390 (36) [ $M^+$  – CO, <sup>187</sup>Re], 388 (23) [ $M^+$  – CO, <sup>185</sup>Re], 362 (60) [ $M^+$  – 2CO, <sup>187</sup>Re], 360 (37) [ $M^+$  – 2CO, <sup>185</sup>Re].

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## Memory of Chirality in Electron Transfer Mediated Benzylic Umpolung Reactions of Arene – Cr(CO)<sub>3</sub> Complexes<sup>\*\*</sup>

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Since the discovery of arene – tricarbonylchromium complexes in 1958<sup>[1]</sup> this class of compounds has been studied extensively. It has been shown that the  $Cr(CO)_3$  group activates the arene ligand in different ways to facilitate transformations that cannot be achieved with the free arenes.<sup>[2]</sup> Furthermore, it has been demonstrated that novel and competitive strategies for the enantioselective synthesis of complex organic molecules are possible if both the chemical and stereochemical properties of such complexes are exploited.<sup>[3, 4]</sup> While the vast majority of applications of arene –  $Cr(CO)_3$  complexes are based on polar reactions involving coordinatively saturated (18 valence electron (VE)) anionic or cationic intermediates,<sup>[2]</sup> it has only recently been realized that transformations involving  $Cr(CO)_3$ -complexed benzylic radicals are also useful for organic synthesis.<sup>[5]</sup>

A theoretical investigation carried out in this laboratory suggests that the parent benzyl radical complex **1a** is better described as the 17 VE resonance structure **1b**. This structure clearly indicates the presence of an exocyclic C–C double bond and shows delocalization of a significant portion of the spin density onto the chromium atom (Scheme 1).<sup>[6]</sup>



Scheme 1. Resonance structures for the Cr(CO)<sub>3</sub>-complexed benzyl radical.

As a consequence, derivatives of **1** that carry an additional substituent in the benzylic position (for example, **2**) are planar chiral radical species and should exhibit a significant degree of configurational stability. Indeed, the barrier for the racemization of **2** was calculated to be 13.2 kcal mol<sup>-1</sup> (Scheme 2),<sup>[7]</sup> which corresponds to a half-life of about one minute at -78 °C.<sup>[8]</sup>

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